TABLE III-6

CORRELATION OF PRODUCTION WITH WATER USE FROM TELEPHONE SURVEY INFORMATION

Production Category, sq ft/day	Water Use Category, gal/day					
	Less than 1,000	1,000 to 9,999	10,000 to 100,000	More than 100,000	Unknown or not given	Total
Less than 1,000	19	11	2	0	3	35
1,000 to 2,999	3	11	3	0	0	17
3,000 to 20,000	2	9	42	4	1	58
More than 20,000	0	0	4	10	2	16
Unknown or not given	0	2	9	0	2	13
Totals	24	33	60	14	8	139

TABLE III-7

CORRELATION OF PROCESS TYPE WITH PRODUCTION FROM TELEPHONE SURVEY INFORMATION

Production, sq ft/day	Black and White Only	Color Negative Only	Color Reversal Only	Color Negative and Reversal	Color and Black and White	Totals
Less than 1,000	16	5	0	1	13	35
1,000 to 2,999	5	5	0	0	7	17
3,000 to 20,000	2	2	7	10	37	58
More than 20,000	0	1	0	2	13	16
Unknown	0	6	0	1	6	13
Totals	23	19	7	14	76	139

TABLE III-8

CORRELATION OF PROCESSING METHODS WITH PRODUCTION FROM TELEPHONE SURVEY INFORMATION

Production, sq ft/day	Machine Processing	Manual Processing	Both Machine and Manual Processing	Totals
Less than 1,000	21	4	10	35
1,000 to 2,999	14	1	2	17
3,000 to 20,000	56	0	2	58
More than 20,000	15	0	1	16
Unknown	11	0	2	13
Totals	117	5	17	139

TABLE III-9

CORRELATION OF REPLENISHMENT USE WITH PRODUCTION FROM TELEPHONE SURVEY INFORMATION

Production, sq ft/day	Used	Not used	Totals
Less than 1,000	32	3	35
1,000 to 2,999	15	2	17
3,000 to 20,000	57	1	58
More than 20,000	16	0	16
Unknown	13	0	13
Totals	133	6	139

TABLE III-10

CORRELATION OF SQUEEGEE USE WITH PRODUCTION FROM TELEPHONE SURVEY INFORMATION

Production, sq ft/day	Everywhere Recommended	Partial	Not Used	Totals
Less than 1,000	11	9	15	35
1,000 to 2,999	10	3	4	17
3,000 to 20,000	52	3	3	58
More than 20,000	16	0	0	16
Unknown	12	1	0	13
Totals	101	16	22	139

TABLE III-11

CORRELATION OF SILVER RECOVERY USE WITH PRODUCTION FROM TELEPHONE SURVEY INFORMATION

Production, sq ft/day	From All Fix Solution Overflows	From Portion of Overflows	Not Used	Totals
Less than 1,000	27	2	6	35
1,000 to 2,999	16	1	0	17
3,000 to 20,000	57	1	0	58
More than 20,000	16	0	0	16
Unknown	13	0	0	13
Totals	129	4	6	139

TABLE III-12

CORRELATION OF SILVER RECOVERY METHODS WITH PRODUCTION FROM TELEPHONE SURVEY INFORMATION

Production, sq ft/day	Metallic Replacement	Electro-lytic	Both Metallic Replacement and Electrolytic	Metallic Replacement and/or Electrolytic and Ion Exchange (resin)	Off Site	None	Totals
Less than 1,000	9	12	5	0	3	6	35
1,000 to 2,999	7	6	4	0	0	0	17
3,000 to 20,000	15	18	24	0	1	0	58
More than 20,000	0	10	4	2	0	0	16
Unknown	6	1	6	0	0	0	13
Totals	37	47	43	2	4	6	139

TABLE III-13

CORRELATION OF BLEACH REGENERATION USE WITH PRODUCTION FROM TELEPHONE SURVEY INFORMATION

Production, sq ft/day	All Bleach Solutions	Portion of Bleach Solutions	Bleaches Used But Not Regenerated	No Bleaches Used	Totals
Less than 1,000	8	5	6	16	35
1,000 to 2,999	9	3	0	5	17
3,000 to 20,000	38	16	2	2	58
More than 20,000	15	0	1	0	16
Unknown	10	2	1	0	13
Totals	80	26	10	23	139

TABLE III-14

CORRELATION OF TREATMENT USE WITH PRODUCTION FROM TELEPHONE SURVEY INFORMATION

Production sq ft/day	Precipitation	Settling	Ozonation	Filtration	Clarification	Aeration Pond	Neutralization	Equalization	Chlorination	Ion Exchange	None	Not Given	Totals
Less than 1,000	0	1	0	1	0	0	0	0	0	0	33	0	35
1,000 to 2,999	0	1	0	0	1	0	1	0	0	0	14	0	17
3,000 to 20,000	4	3	1	1	1	0	2	1	1	0	43	3	60
More than 20,000	3	0	1	0	0	1	1	0	0	1	7	3	17
Unknown	0	0	0	0	0	0	0	0	0	0	13	0	13
Totals	7	5	2	2	2	1	4	1	1	1	110	6	142*

* Total number of plants greater than 139 indicates double accounting.

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TABLE III-15

CORRELATION OF DISCHARGE METHOD WITH PRODUCTION FROM TELEPHONE SURVEY INFORMATION

Production sq ft/day	POTW	Direct	Separated Waste Streams Both POTW and Direct	POTW and Contract Haul	Percolation-Evaporation Pond	Unknown	Totals
Less than 1,000	29	3	0	1	1	1	35
1,000 to 2,999	16	1	0	0	0	0	17
3,000 to 20,000	53	2	1	1	0	1	58
More than 20,000	10	1	1	1	0	3	16
Unknown	10	0	1	1	0	1	13
Totals	118	7	3	4	1	6	139

SECTION IV

INDUSTRY CATEGORIZATION

INTRODUCTION

The purpose of industry categorization is to establish subcategory groupings for pollution control purposes within the photographic processing industry such that plants within each group have an equal ability to meet the established effluent limitations guidelines. Upon examination of the various categorization bases it was determined that this industry should be considered as a single group. The following subsection describes the considerations for making this determination.

CATEGORIZATION BASIS

After considering the nature of the various segments of the photographic processing industry and the operations performed therein, the following factors were considered as bases for subcategorization:

1. Process type
2. Service performed or customer type
3. Type and quantity of material processed
4. Age of facility and number of employees
5. Geographic location
6. Water use
7. Effluent discharge destination

Process Type

Since the processes performed in a plant are the sources of wastes from a plant, the photographic processes would seem to be a natural candidate for subdividing the industry. As described in Section III, there are a number of process types used.

Many of the plants surveyed use multiple process types for processing a mixture of photographic materials. The mixed wastes from these plants tend to blend any distinguishing process characteristics. There are, of course, plants where

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wastes do not contain all of the pollutant parameters of concern because only one process type is used or the process blend is such that one or more of the waste parameters of concern is omitted. For example, a black and white negative only plant does not use bleach, and a color negative only plant typically does not use ferricyanide or dichromate bleach. (The color negative process, MC-42, uses ferricyanide bleach, but observations during the study showed a tendency for color negative and print plants to use the C-41 process which uses a ferric EDTA bleach. The MC-42 process is more likely to be used in plants having a mix of reversal processes and use a house ferricyanide bleach system.) As a result, total cyanide and chromium pollutants are not added to the wastewater and these plants will have no difficulty in meeting any limitation on these pollutant parameters. Therefore, the presence or absence of certain process types is not a basis for subcategorization.

Service Performed or Customer Type

The service performed or customer type determines the types of materials to be processed which, in turn, determines the processes utilized. Therefore, the above discussion about process type is also applicable to the service performed.

Type and Quantity of Material Processed

Some distinguishing process characteristics for the various material types are shown in Table IV-1.

TABLE IV-1
Distinguishing Process Characteristics of Various Material Types

Material Type	Processing Characteristics
Black and White	
Negative	No bleach
Reversal	Dichromate bleach, waste bleach contains silver
Color Film	
Negative	High silver, ferricyanide or EDTA bleach
Reversal	High silver, ferricyanide, EDTA, or ferric chloride bleach
Negative, movie	High silver, ferricyanide bleach
Negative, movie print	Low silver, dichromate or ferricyanide bleach
Color Paper	
Negative	Low silver, EDTA bleach
Reversal	Low silver, EDTA bleach

As indicated, some of the materials have a relatively high or low amount of silver in the emulsion that is potentially released to the wastewater. Generally, most plants process a mixture of materials which tend to produce an amount of silver in the effluent per production unit that is in the mid-range of silver that would come from film or paper alone. For example, it is common for a plant to process both film (high silver) and paper (low silver). Even a movie film plant which processes all film is analogous to the common film-paper plant in that the movie plant processes both high silver content negatives and low silver print film. A plant which processes only reversal films will have a relatively high silver load prior to silver recovery. Silver recovery processes are generally operated to reduce silver concentrations to comparable levels regardless of the silver concentration before silver recovery. So, assuming similar hydraulic loads, a reversal only plant would potentially have effluent silver levels equivalent to those of other types of plants.

The bleach characteristics in Table IV-1 are related to process type; therefore, the discussion on process types is applicable.

Production normalized quantities of process water and silver in the effluent versus the quantity of material processed (production) are shown in Figures IV-1 and IV-2, respectively, for the plants studied. The plants having end-of-pipe treatments are identified in Figure IV-2.

The water use plot indicates no strong dependency of water use with production, and the plot of silver load versus production shows a general downward trend of lower silver with increased production. However, when considering the grouping of plants with similar silver treatment, the grouped silver quantities are generally independent of production. The downward trend is most likely a result of increased silver treatment rather than a dependency on production. Water use may be higher in plants with production of less than 93 sq m/day (1,000 sq ft/day) due to inefficiencies of operation and the use of less efficient (in terms of water use) process equipment, but the available information is insufficient to make this determination. Therefore, based on available information, processed material quantity is not a suitable parameter for subcategorization.

Age of Facility

Production normalized quantities of process water versus plant age and silver in the effluent versus plant age are shown in Figures IV-3 and IV-4, respectively, for the plants studied. No particular relationship between these parameters is shown, and therefore plant age is not a suitable basis for subcategorization.

Number of Employees

Production normalized quantities of process water versus number of employees and silver in the effluent versus number of employees are shown in Figures IV-5 and IV-6, respectively, for the plants studied. No particular relationship between these parameters is shown, and therefore number of employees is not a suitable basis for subcategorization.

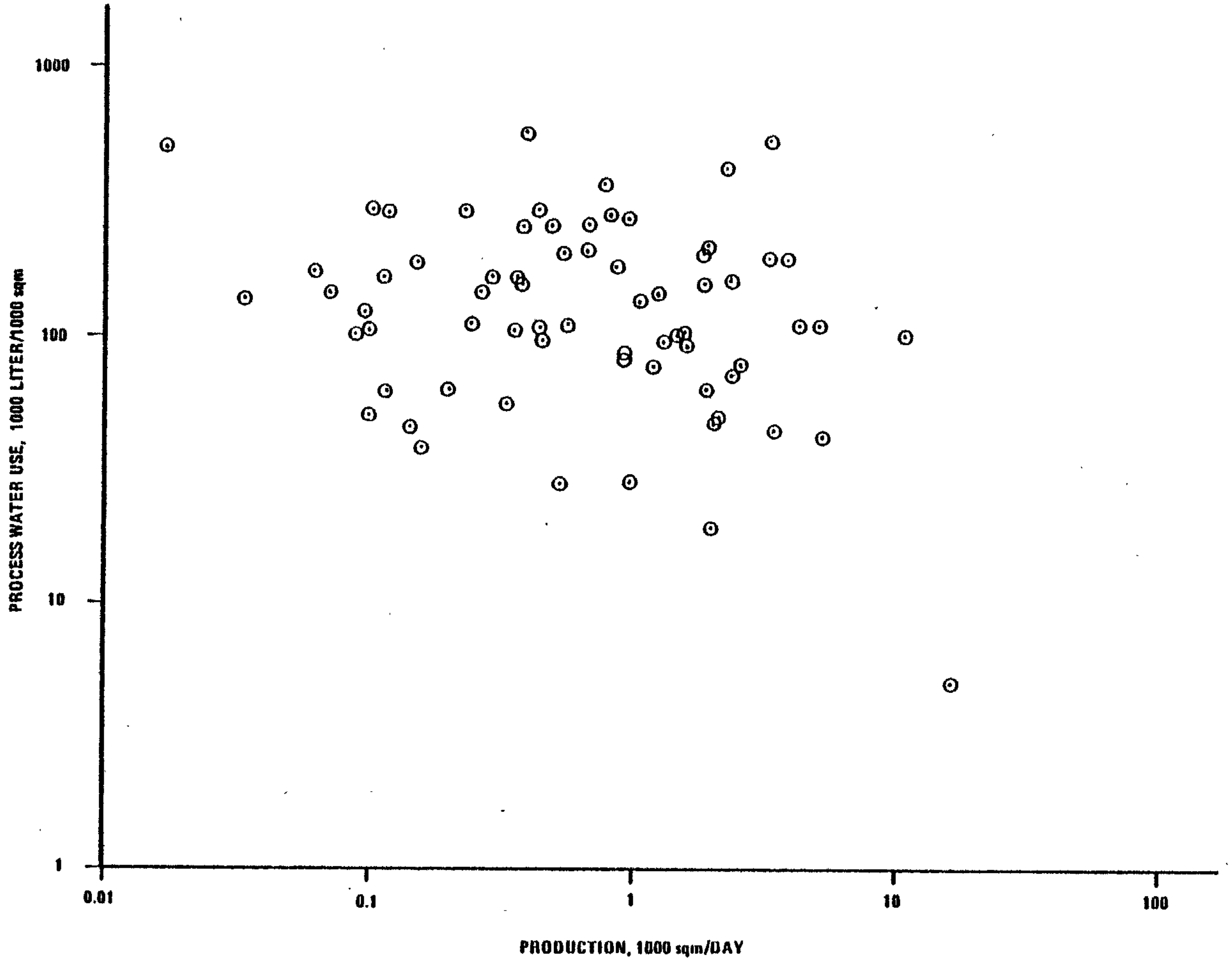

FIGURE IV-1 PROCESS WATER USE VS. PRODUCTION

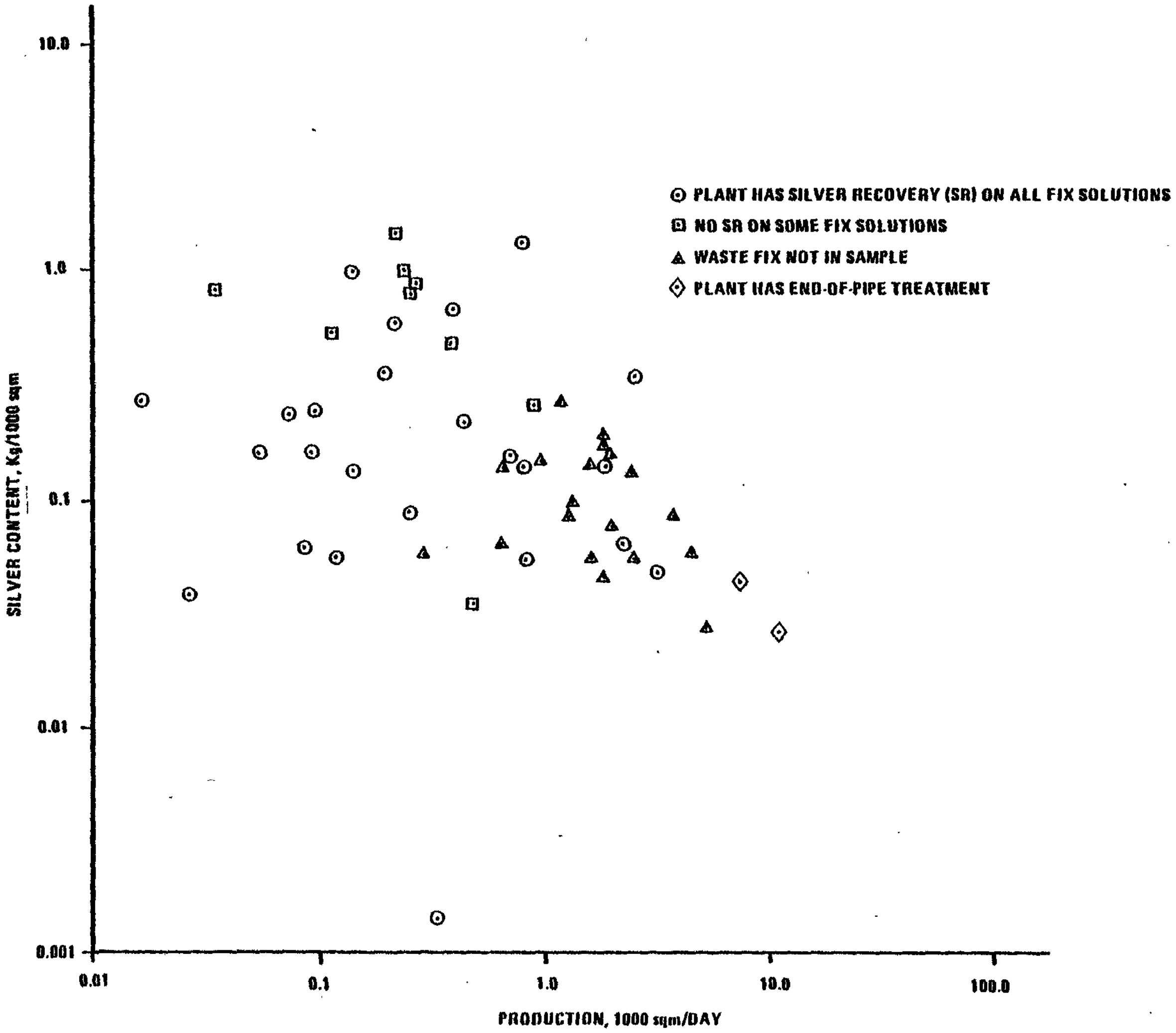

FIGURE IV-2 AMOUNT OF SILVER IN EFFLUENT VS. PRODUCTION

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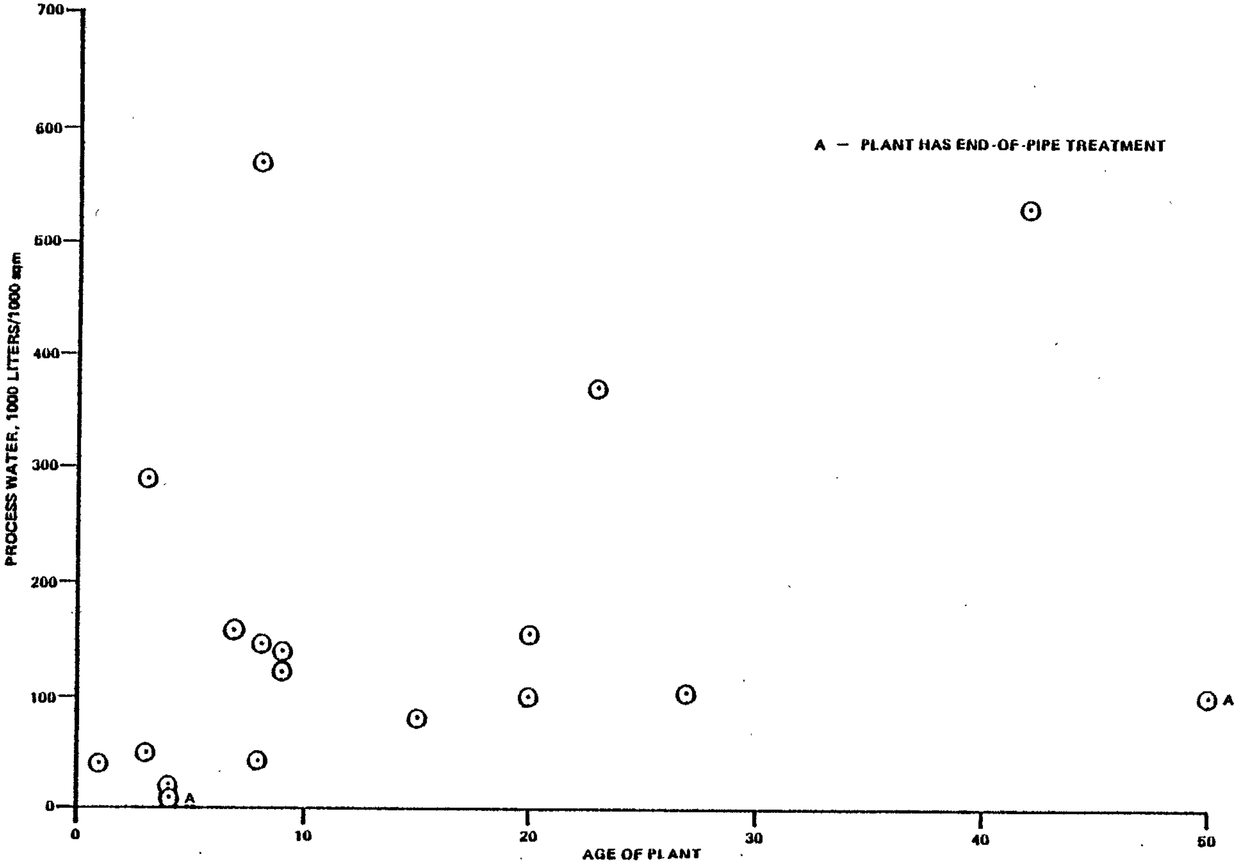

FIGURE IV-3 AGE OF PLANT VS. PROCESS WATER USE

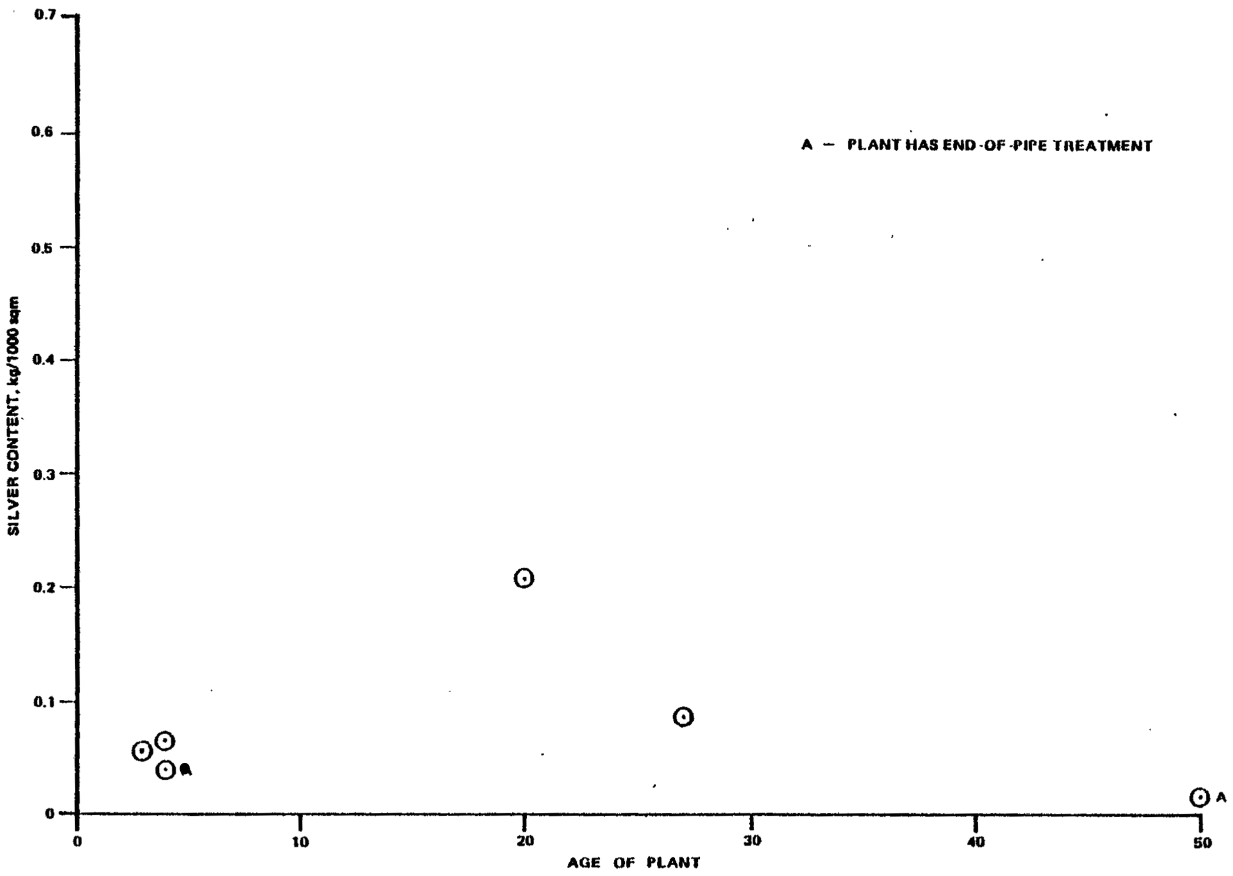

FIGURE IV-4 AGE OF PLANT VS. AMOUNT OF SILVER IN EFFLUENT

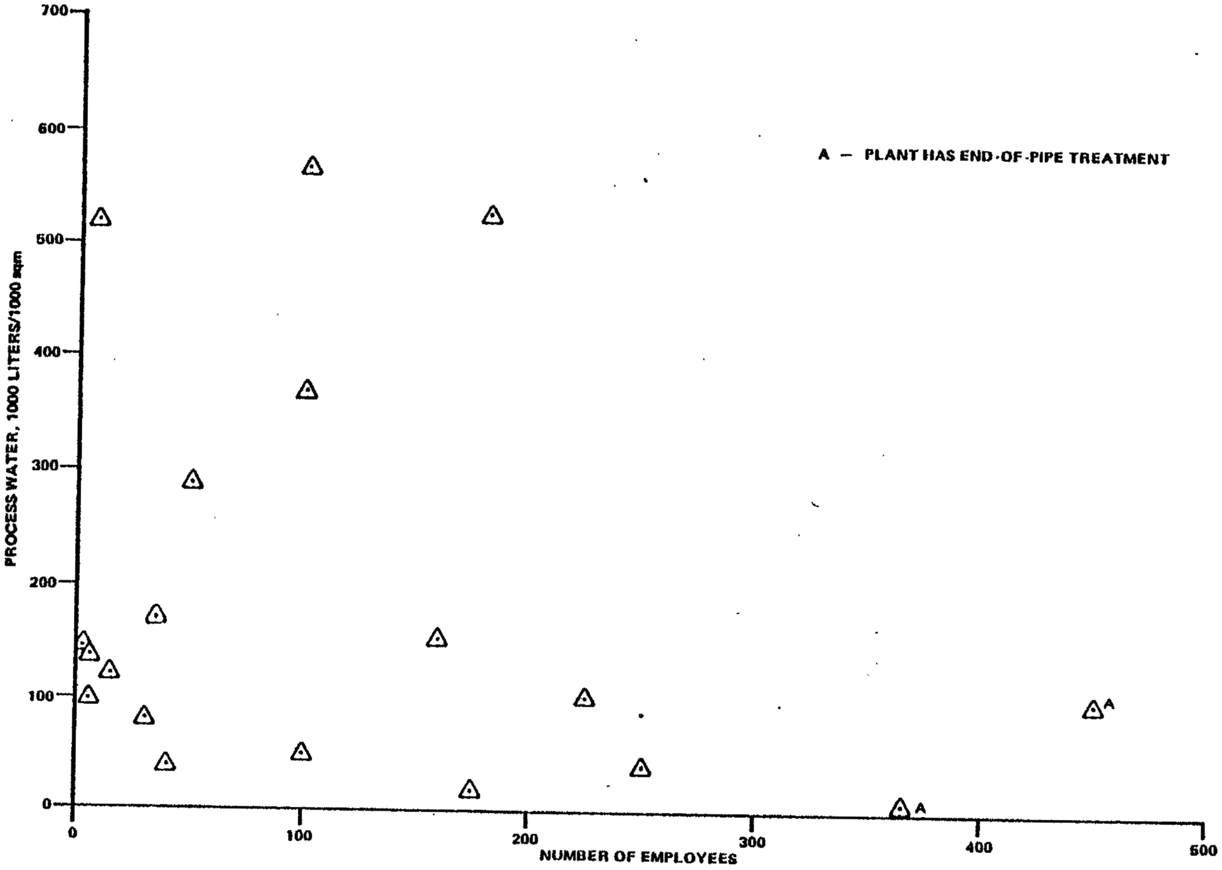

FIGURE IV-5 NUMBER OF EMPLOYEES VS. PROCESS WATER USE

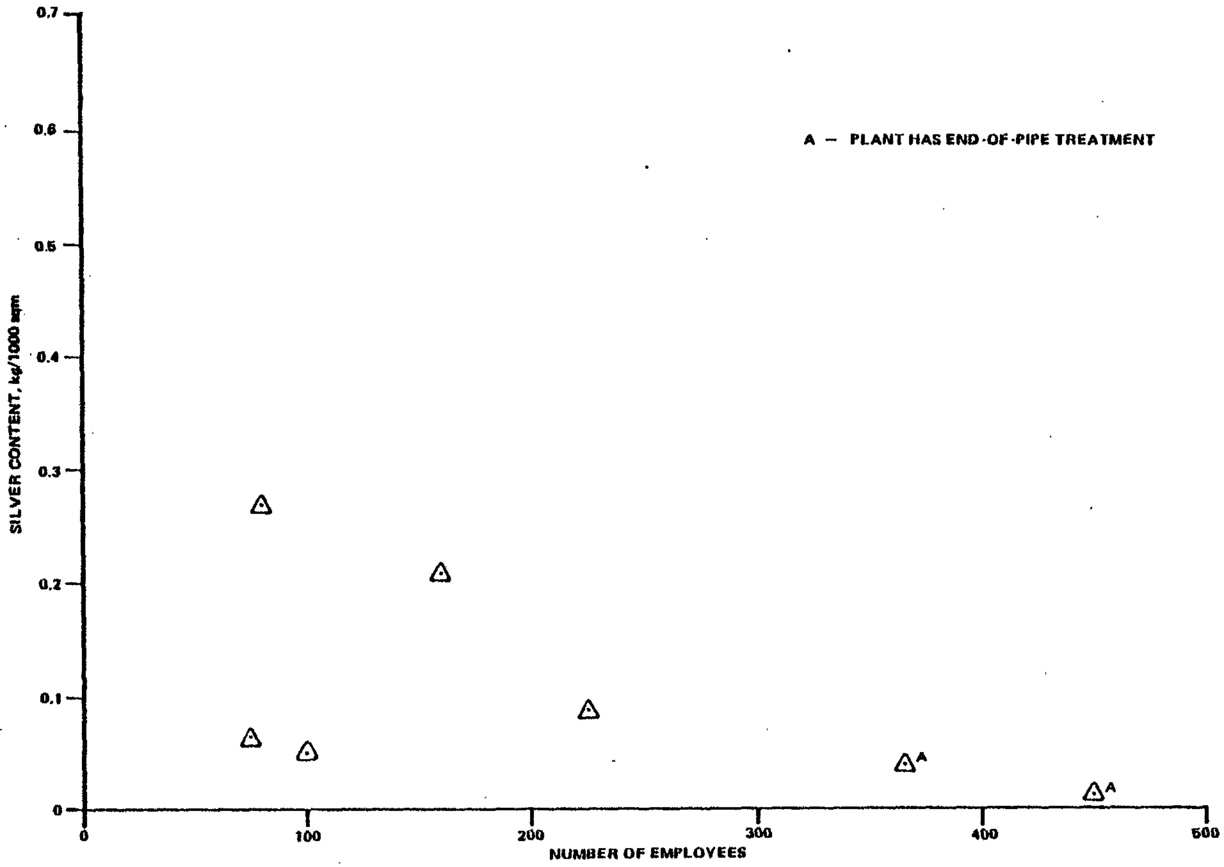

FIGURE IV-6 NUMBER OF EMPLOYEES VS. AMOUNT OF SILVER IN EFFLUENT

Geographic Location

Geographic location is not a basis for subcategorization. Photographic processes are not affected by the physical location of the facility. The price or availability of water may affect the amount of modification to procedures used in each plant. However, procedural changes to conserve water can affect the concentration of pollutants discharged but not the amount or characteristics of the constituents. The waste treatment procedures described in Section III can be utilized in any geographical area. In the event of a limitation in the availability of land space for constructing a waste treatment facility, the in-process controls and wash water conservation techniques described in Section III can be adopted to minimize the land space required for the end-of-process treatment facility. Often, a compact package unit can easily handle end-of-process waste, if good in-process techniques are utilized to conserve raw materials and water.

Water Use

As previously shown in Figure IV-1, no strong dependency exists between water use and plant size in terms of the quantity of material processed. It is expected that the relative amount of water used by very small plants, less than 93 sq m/day (1,000 sq ft/day), will be larger than the industry norm due to inefficiencies of operation. For example, when production is low, process machines may be on stand-by for long periods during which time there is some wash water flow. Small processors commonly use manual tray processing and low volume production sheet film and paper processors which are inherently less efficient in water use than large continuous process machines. The available data are insufficient to quantify the water use for these very small plants. For the size of plants represented in Figure IV-1, there is no basis for subcategorization.

Effluent Discharge Destination

Of the approximately 11,000 photographic processing dischargers, fewer than 20 are direct dischargers as determined by an NPDES permit search. The fact that a plant is a direct discharger has no effect on the type of pollutants discharged. Direct dischargers may currently have more stringent limitations because of permit requirements. As a result, they may have applied more effective controls and thus have smaller pollutant amounts than those which discharge to POTWs. The available data are insufficient to make this determination.

SELECTION OF PRODUCTION RELATED PARAMETER

In the selection of a suitable production normalizing parameter, a number of production related factors were considered. The level of production activity in a particular plant can be expressed as the processed area, raw materials consumed, number of process machines, or number of employees.

All of these parameters have some relation to the level of production in a particular plant, but area processed is more closely associated with the level of activity relative to pollutant discharge than the other parameters for the photographic industry. Raw material consumed is directly related to area processed but with the area being the primary factor. The number of process machines is related to the area processed but varies depending upon the degree of utilization of each machine in a particular plant. The number of employees is an unreliable measure of production because of a varying degree of automation, particularly in the smaller facilities. Therefore, the area of emulsion processed was selected as the production normalizing parameter.

SECTION V

PROCESS WASTE CHARACTERIZATION

DATA BASE

The initial EPA study of the Photographic Processing Industry was conducted during the period mid-1974 through mid-1976 and included a Kodak "200 plant" survey and the collection of data and sampling of three plants in the fall of 1974. In the spring of 1976 the National Association of Photographic Manufacturers (NAPM) conducted a sampling effort of 37 plants. An expanded EPA effort was initiated in the fall of 1976 for the purpose of collecting additional information. This second EPA study began in October 1976 with the sampling of two plants. Then information was obtained from 139 plants in a telephone survey which was described in Section III. A formal request for data was made to those plants which indicated during the telephone survey that they had available self-monitoring data on wastewater characteristics. A total of 19 plants submitted some information based on this request. From information gathered in the telephone survey, twenty plants were selected and visited. Detailed engineering information was obtained on the process water use, in-process controls, end-of-pipe treatments and wastewater characteristics. The factors considered during the selection process were product mix, in-process controls, end-of-pipe treatments, size (production) and data availability. Primary consideration was given to the use of end-of-pipe treatments and in-process controls. Five of the 20 plants visited were selected for sampling by EPA. Selection factors considered were product mix, in-process controls and end-of-pipe treatments. The sampling of these plants took place in the summer of 1977. A summary of these data sources is given below:

Information Source and Type	Number of Plants
1969-1974 Kodak "200 Plant" Survey	237
1974 - EPA Engineering Plant Visit and Sampling	3
1976 - NAPM Sampling	37
1976 - EPA Sampling	2
1976 - EPA Telephone Survey	139
1976 - EPA Engineering Plant Visit	20
1977 - EPA Sampling	5
1976 - Self-monitoring data submitted to EPA on request	17

Note that some plants in each source category may be included in another category. For example, some of the 37 plants in the NAPM sampling effort were also covered in the 139 plant telephone survey.

Section V contains data for 76 plants obtained from the described sources of information. Four digit number codes are used to represent each of the studied plants. The series of numbers 02nn have been assigned to the 37 plants included in the 1976 NAPM sampling effort. The data have been condensed (by averaging) and abridged. Table V-1 lists the plants studied by plant code and gives some general characteristics of their customer type, SIC code, relative size, and production. The production information is given in terms of percent film production, percent black and white production, and the percentage of color production attributed to the several bleach types.

Sampling Efforts

EPA conducted waste stream sampling efforts in the fall of 1974 and 1976 and in the summer of 1977. A major portion of the 1977 effort was devoted to the sampling and analyses for priority pollutants. The collected effluent samples consisted of flow proportioned composites taken during single process days in the 1974 and 1976 sampling efforts. Flow proportioned composites were taken for each of three days at each site during the 1977 sampling effort with the exception of plants 2714 and 9026. No effluent samples were

TABLE V-1

PRODUCTION SUMMARY

Plant Code	Customer Type	SIC	Size	Percent* Black and White Production	Percent Film Production	Percent Ferricyanide Production	Percent Ferric EDTA Production	Percent Dichromate Production
0021	AM	7395	C	0	15	1	99	0
0045	AM	7395	B	8	14			0
0118	COM	7333	C	0	40	15	85	0
0201	α	α	A	0	α	11	89	0
0202	AM-PRO	7395	<A	0	α	0	100	0
0203	AM	7395	A	α	α	0	α	0
0204	AM	7395	C	α	α	1	α	0
0205	MOV	7819	C	α	α	15	α	α
0206	AM-PRO	7395	B	0	α	0	100	0
0207	PRO	7395	A	0	α	0	100	0
0208	AM	7395	C	0	α	α	α	0
0209	AM-PRO	7395	A	α	α	0	α	0
0210	SCH	7221	B	0	α	1	99	0
0211	AM-PRO	7395	A	0	α	0	0	0
0212	AM	7395	<A	0	0	0	100	0
0213	α	α	B	α	α	0.3	α	0
0214	AM	7395	<A	0		0	100	0
0215	AM	7395	C	α	α	1	α	0
0216	AM	7395	<A	α	α	0	α	0
0217	AM	7395	C	α	α	1	α	0
0218	AM	7395	B	α	α	2	α	α

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* All percentages are percent of total production
α Not given and/or cannot be estimated from processes used

CUSTOMER KEY:

AM - Amateur
AER- Aerial
COM- Commercial
GOV- Government
MIL- Military
MOV- Movie
PTS - Portrait Studio
PRO - Professional
SCH - School
X-R - Industrial X-Ray

SIZE KEY:	Production, sq m/day (sq ft/day)
<A	<93 (<1,000)
A	93-186 (1,000-2,000)
B	186-464 (2,000-5,000)
C	464-4,640 (5,000-50,000)
D	4,640-∞ (50,000-∞)

TABLE V-1
(continued)

Plant Code	Customer Type	SIC	Size	Percent* Black and White Production	Percent Film Production	Percent Ferricyanide Production	Percent Ferric EDTA Production	Percent Dichromate Production
0219	AM	7395	C	α	α	2	α	α
0220	α	α	A	0		0	100	0
0221	MOV	7819	B	0	100	α	0	α
0222	AM	7395	B	0	α	α	α	0
0223	AM	7395	C	0	α	0.3	α	0
0224	α	α	A	0	α	0	100	0
0225	AM	7395	C	α	α	α	α	α
0226	AM	7395	A	0	α	0	100	0
0227	MOV	7819	B	α	100	22	α	α
0228	MOV	7819	C	0	100	1	α	α
0229	α	α	<A	α	α	5	α	α
0230	AM	7395	B	α	α	α	α	0
0231	MOV	7819	C	0	100	α	0	α
0232	AM	7395	C	0	100	100	0	0
0233	AM	7395	C	0	100	100	0	0
0234	AM	7395	C	0	100	100	0	0
0235	AM	7395	C	0	100	100	0	0
0236	AM	7395	C	0	100	100	0	0
0237	AM	7395	C	0	100	100	0	0
0662	AM	7395	C	0	15	1	99	0

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* All percentages are percent of total production

α Not given and/or cannot be estimated from processes used

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AM - Amateur
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MOV - Movie
PTS - Portrait Studio
PRO - Professional
SCH - School
X-R - Industrial X-Ray

SIZE KEY: Production, sq m/day (sq ft/day)

<A <93 (<1,000)
A 93-186 (1,000-2,000)
B 186-464 (2,000-5,000)
C 464-4,640 (5,000-50,000)
D 4,640-∞ (50,000-∞)

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TABLE V-1
(continued)

Plant Code	Customer Type	SIC	Size	Percent* Black and White Production	Percent Film Production	Percent Ferricyanide Production	Percent Ferric EDTA Production	Percent Dichromate Production
1232	SCH	7221	C	10	1.3	0	90	0
1421	COM	7333	<A	50	18	10	40	0
1465	AM	7395	C	6	11	3	91	0
1635	AM	7395	C	0	15	1	99	0
2146	AM	7395	C	16	33	α	α	0
2387	X-R	7333	<A	100	100	0	0	0
2465	AM	7395	C	23	64	77	0	0
2488	AM	7395	C	0	100	100	0	0
2714	AM	7395	C	0	22	0.4	99.4	0
2892	GOV	7333						
3075	PRO	7395	B	89	7	2	9	0
3437	AM	7395	C	0	29	100	0	0
3455	AM	7395	C	0	95	95	5	0
3630	AM	7395	C	0	15	1	99	0
4228	AM	7395	C	9	98	91	0	0
4229	AER	7333	<A	100	62	0	0	0
4550	AM	7395	C	0	28	28	72	0
4666	AM	7395	C	0	100	100	0	0
4849	MIL	7333	B	14	93	21	3	63 ϕ
5120	AM	7395	B	0	5	0	100	0

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* All percentages are percent of total production
α Not given and/or cannot be estimated from processes used
ϕ Dichromate from movie production

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AM - Amateur
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MOV - Movie
PTS - Portrait Studio
PRO - Professional
SCH - School
X-R - Industrial X-Ray

SIZE KEY: Production, sq m/day (sq ft/day)

<A	<93 (<1,000)
A	93-186 (1,000-2,000)
B	186-464 (2,000-5,000)
C	464-4,640 (5,000-50,000)
D	4,640-∞ (50,000-∞)

TABLE V-1
(continued)

Plant Code	Customer Type	SIC	Size	Percent* Black and White Production	Percent Film Production	Percent Ferricyanide Production	Percent Ferric EDTA Production	Percent Dichromate Production
5359	X-R	7333	B	100	73	0	0	0
5552	AM	7395	C	43	100	57	0	0
6174	AM	7395	C	0	11	2	98	0
6208	MOV	7819	D	4	100	4	0	92
6237	AM	7395	D	3	26	17	80	0
6443	AM	7395	D	∝	∝	∝	∝	∝
6582	AM	7395	C	0	15	1	99	0
6726	AM	7395	C	8	53	92	0	0
7644	AER	7333	A	80	44	7	13	0
7781	PTS	7221	D	0	2.5	0	100	0
8058	PRO	7395	A	0	8	0	100	0
8226	MOV	7819	C	3	100	15	0	82
9061	MOV	7819	C	1	100	14	0	86
9297	GOV	7333	B	75	53	10	16	0
9942	COM	7333	C	0	40	15	85	0

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* All percentages are percent of total production

∝ Not given and/or cannot be estimated from processes used

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MOV - Movie
PTS - Portrait Studio
PRO - Professional
SCH - School
X-R - Industrial X-Ray

SIZE KEY: Production, sq m/day (sq ft/day)

<A	<93	(<1,000)
A	93-186	(1,000-2,000)
B	186-464	(2,000-5,000)
C	464-4,640	(5,000-50,000)
D	4,640-∞	(50,000-∞)

taken at 9026; only grab samples were taken from two silver recovery units. The waste stream samples at plant 2714 were collected in 38,000 liter (10,000 gal) tanks prior to discharge. Grab samples were taken from these tanks when they were essentially full.

Plants 4550, 6237 and 1465 were sampled by EPA in the fall of 1974. Plant 4550 was re-sampled in 1977 and the more current data are included in this report. Plant 6237 discharged treated wash water directly to surface waters and concentrated chemicals to a POTW at the time of sampling. Since that time, the plant has combined the waste streams and is discharging to a POTW without end-of-pipe treatment. The data are no longer representative of the plant's operation. Plant 1465 also separates the wash water from the concentrated chemical wastes. The wash water, mixed with some non-contact cooling water, is discharged directly to surface waters without treatment. The concentrated chemicals waste stream is treated and discharged to a POTW. The data for these two streams have been combined and appear later in this section under Effluent Characteristics After End-of-Pipe Treatments.

Plants 6443 and 2488 were sampled by EPA in September 1976. Samples were split with each plant, and the reported pollutant concentrations are averages of the results obtained by the plant and EPA with a few exceptions. The silver value obtained by plant 2488 is reported and the cyanide value obtained by EPA at 6443 is reported. These individual results are more consistent with historical data from similar plants. Both plants use silver recovery and bleach regeneration on all applicable solutions. Plant 2488 treats fix waste by precipitation with ferrous sulfate in a batch operation for cyanide reduction before discharge. No batches were treated and discharged during the sampling period so that the sample taken includes no fix waste except for that carried over into the wash water. Such fix waste is included in the EPA sample from plant 4550. This plant is similar in process and waste handling characteristics to plant 2488. The data for plant 4550 effluent containing the waste fix also appear later in this section.

The samples collected during the 1977 EPA sampling efforts were split with NAPM. The pollutant parameter concentration values reported in the following data tables are an average of the EPA and NAPM values with the exception of certain parameters measured in the concentrated process solutions (before in-process controls). Because of the concentrated chemical content of these solutions, various chemical interferences caused some inconsistencies in the results between the two labs. The NAPM values for total cyanide and silver were, in general, used for the concentrated solutions. These selections were necessary because it was found that the standard EPA procedures did not consistently give reasonable results for those concentrated chemical solutions. NAPM used modified or other standard test procedures in these cases based on their experience with photographic solutions and obtained results more consistent with the known solution formulations. The following is a brief description of the major modifications made by NAPM on the test procedures.

Total cyanide - In the presence of reducing agents such as sulfites and thiosulfates, an excess of chloramine T is required. After distillation, a determination was made of the amount of reducing agent present. The amount of chloramine T added depended on this result. The EPA procedure calls for a fixed amount.

Silver - On concentrated samples NAPM used long digestion periods of 0.5 to 3 hours with one hour typical. Nitric-sulfuric acid was added during digestion to prevent dryness. EPA digested directly to dryness in considerably less time, potentially resulting in incomplete digestion and low values.

NAPM conducted their own sampling effort in the spring of 1976. The results include 31 plants sampled for two days in 1976 and 6 plants sampled at various times during the period 1973-1976. Each sample is a flow proportioned composite taken from the plant discharge during the daily production period. In some cases the tested samples contain sanitary wastewater. None of these plants use end-of-pipe treatment prior to discharge except plants 32 through 37 which treat waste fix for removal of ferri/ferrocyanide before discharge; however, no treated waste fix was discharged during sampling.

In this section, all production related parameters are expressed in terms of surface area of photographic emulsion processed in units of thousand square meters with corresponding English units of thousand square feet in parentheses.

PROCESSES USED

The processes used by the plants studied are listed in Table V-2. Details of the listed processes were discussed in Section III. In general, the process chemistry and procedure at each plant were the same as that previously described. The variances observed were minor, usually involving wash steps. The number and placement of some wash steps are somewhat dependent upon the type of process machine and squeegee usage. In black and white processing it was common for the stop step to be eliminated. Sometimes a hypo eliminator or hypo clearing agent step was added after fix. Because of the more complicated chemical reactions and critical controls necessary for color processing, there is very little latitude for process variance. Although it is possible to substitute ferricyanide bleach for the prescribed EDTA bleach in the C-41 process, no plants studied made this change. Plant 1232 uses EP-3 chemistry for color paper processing but has eliminated the stabilization step. The process, then, is essentially identical to EP-2 which has no stabilizer step. Plant 3075 uses a bleach-fix in the C-41 and C-22 processes for which separate bleach and fix solutions are prescribed, the bleaches being EDTA and ferricyanide, respectively. This substitution is unusual but both processes had very limited usage.

A list of the plant in-process controls used by plants studied is given in Table V-3. The silver recovery usage column refers to waste fix where "all" means that silver is recovered from each fix solution from each process line. In the primary silver recovery column, the notation "B In-line" refers to a circulating fix solution system where an "in-line" electrolytic silver recovery unit continuously recovers silver from the fix.

Plants 6208 and 7781 recover silver from the after-fix wash waters and recycle a portion of the de-silvered water to process use. Plant 6208 uses an ion exchange system to recover silver from a mixture of waste fix and wash water. A portion of the treated water is chlorinated and recycled

TABLE V-2
PHOTOGRAPHIC PROCESSES USED AT PLANTS STUDIED

PROCESS \ PLANTS	0021	0045	0118	0662	1232	1421	1465	1635	2146	2387	2465	2488	2714	2892	3075	3437	3455	3630	4228
Black and White Negative																			
Film		X			1	(1)	1		X	3	X			1	1(1)				X
Paper		X			3	1(1)	2		X					1	1(3)				
Color Negative Film																			
C-22	X			X		1	1	X	X		X		1		(1)	X		X	
C-41	X		X	X	1	(1)	3	X					3		1			X	
MC-42											X					X			
ECP-1																			
ECN-1											X					X			
ECN-2																			
MN-31		X																	
Color Negative Paper																			
EP-2	X			X	2	1		X			X		4			X		X	X
EP-3		X	X				3		X										
MC-111															1				
85/86																			
Color Reversal Film (IC)																			
E-3			X			1													
E-4							1		X		X	X				X	2		X
ME-4											X	X							X
EM-25							1				X	X				X	2		X
E-7M																X			
EA-5														1					
CRI																			
ECO-3											X								X
E-2															1(2)				
Color Reversal Paper (IC)																			
EPR-5									X								1		
Type A							1												
Cibachrome														1					
Color Reversal Film (DC)											X	X							X
K-12																X	3		
K-14									X		X	X				X	3		X

NOTE: "X" represents presence of machine process lines, and numbers represent number of machine process lines of each plant. Some machines are capable of processing multiple strands. Numbers in parentheses ( ) represent manual process lines. Not all listed process lines are necessarily in operation every day.

TABLE V-2
(continued)

PROCESS \ PLANTS	4229	4550	4666	4849	5120	5359	5552	6174	6208	6237	6443	6582	6726	7644	7781	8058	8226	9061	9297	9942
Black and White Negative																				
Film	(1)			4		1	X		3	1	X		X	3			X*	1	3	
Paper	1			1		1				1	X			1					1	
Color Negative Film																				
C-22				(1)				2		1	X	X	X							
C-41		1			X			2		3	X	X		1		1				X
MC-42		1					X						X							
ECP-1				2					8								X	3		
MN-31																		2		
ECN-2									2						1			2		
Color Negative Paper																				
EP-2		2						4		1		X	X	1		2				
EP-3				1							X									X
MC-111																				
85/86					X					3					4					
Color Reversal Film (IC)																				
E-3				(1)																X
E-4		1	X	1			X			1			X							
ME-4			X	1			X										X			
EM-25		1	X				X			1	X		X							
E-7M		1	X																	
EA-5																			2	
CRI									1									1		
ECO-3				1			X													
E-2																				
Color Reversal Paper (IC)																				
EPR-5		1									X		X						1	
Type A																				
Cibachrome														1						
Color Reversal Film (DC)							X													
K-12													X							
K-14		3	X				X			2			X							

NOTE: "X" represents presence of machine process lines, and numbers represent number of machine process lines of each plant. Some machines are capable of processing multiple strands. Numbers in parentheses ( ) represent manual process lines. Not all listed process lines are necessarily in operation every day.

* Includes black and white reversal film.

TABLE V-2
(continued)

PROCESS \ PLANTS	0201	0202	0203	0204	0205	0206	0207	0208	0209	0210	0211	0212	0213	0214	0215	0216	0217	0218	0219	0220
Black & White Negative																				
Film			1	1	1				1				1		1	1		1	1	
Paper				1					1				1		1		1	1	1	
Color Negative Film																				
C-22	1			1				1		1					1		2	2	3	
C-41		2	2	2		2	1	3	2		2		2	1	2	1	3	2	3	1
MC-42																				
ECP-1					1															
ECN-1																				
ECN-2																				
Color Negative Paper																				
EP-2									2											
EP-3	1	1	1	1		3	1	5		3	2	1	2	1	1		5	1	4	1
MC 111																				
85/86																				
Color Reversal Film (IC)																				
E-3																				
E-4													1							
ME-4					1															
EM-25								1												
E-7M																				
EA-5																				
CRI																				
ECO-3					1															
VNF					1															
Color Reversal Paper (IC)																				
EPR-5					1			1												
Type A																				
Cibachrome																				
Color Reversal Film (DC)																				
K-12																				
K-14																				

NOTE: Numbers represent number of machine process lines of each plant. Some machines are capable of processing multiple strands. Numbers in parentheses ( ) represent manual process lines. Not all listed process lines are necessarily in operation every day.

TABLE V-2

(continued)

PLANTS / PROCESS	0221	0222	0223	0224	0225	0226	0227	0228	0229	0230	0231	0232	0233	0234	0235	0236	0237
Black & White Negative																	
Film					1		1		1	1							
Paper					1				1	1							
Color Negative Film																	
C-22		1	1						2	1	1		2	2			
C-41		3	2	1	2	1				2							
MC-42													1	1			
ECP-1	1						1	2			2						
P-124													2	1			
MN-31													1	1			
ECN-2							2				1						
Color Negative Paper																	
EP-2			2														
EP-3		3		1	2	3			1	2							
MC 111																	
85/86																	
Color Reversal Film (IC)																	
E-3																	
E-4									1			2	2	2	2	1	2
ME-4								1				1		2	2	2	1
EM-25												1	1	1	1	1	1
E-7M																	
P-112														1			
CRI											1						
ECO-3							1										
Color Reversal Paper (IC)																	
EPR-5					2												
Type A																	
Color Reversal Film (DC)																	
K-12												3	4	3	3	3	3
K-14												2	2	3	1		2
RCP-2														1	2	2	1

NOTE: Numbers represent number of machine process lines of each plant. Some machines are capable of processing multiple strands. Numbers in parentheses ( ) represent manual process lines. Not all listed process lines are necessarily in operation every day.

TABLE V-3

RECOVERY AND REGENERATION AT PLANTS STUDIED

	SILVER RECOVERY			BLEACH REGENERATION					DEVELOPER		WASH WATER SILVER RECOVERY
		METHODS			METHODS						
Plant Code	Usage	Primary	Tailing	Usage	Ferri-cyanide	EDTA	Chromate	Bleach-Fix	Coupler Recovery	Regener-ation	Method
0021	All	A,B	A	All	D	G	NA	F	NA	X	None
0045	All	A	None	All	NA	F	NA	F	NA	X	None
0118	All	A	None	Partial	X	F	NA	F	NA	X	None
0662	All	A,B	A	All	D	G	NA	F	NA	X	None
1232	All	A	None	All	NA	F	NA	F	NA	X	None
1421	All	A,Y	None	Partial	X	F	NA	F	NA	X	None
1465	All	A,B	A,B	Partial	X,E	G	NA	F	NA	X	None
1635	All	A,B	A	All	D	G	NA	F	NA	X	None
2146	All	A,B	NG	All	D	F	NA	F	H	X	None
2387	All	B In-Line	B	NA					NA	X	None
2465	All	A,B	B	All	D	NA	NA	NA	H	X	None
2488	All	A,B	B	All	D	NA	NA	NA	H	X	None
2714	All	A,B	A	All	D	G	NA	F	NA	X	None
2892	Partial	A,B, B In-Line	B	Partial	B	NA	NA	NA	NA	X	None
3075	Partial	A,B,Y	None	None	X	X	NA	X	NA	X	None
3437	All	A,B	B	All	D	NA	NA	NA	H	X	None
3455	All	A,B In-Line	B	All	E	NA	NA	F	H	X	None
3630	All	A,B	A	All	D	G	NA	F	NA	X	None
4228	All	A,B	B	All	D	NA	NA	NA	H	X	None

KEY:

A - Metallic Replacement
B - Electrolytic
C - Resin Ion Exchange
D - Persulfate
E - Ozone
F - Aeration and Chemical Addition
G - Chemical Addition
H - Acidify with Sodium Bisulfate
I - Acidify with Carbon Dioxide
J - Reverse Osmosis
K - Precipitation and Settling
NA - Not Applicable
X - Used and Not Regenerated
Y - Off-Site Recovery
NG - Not Given

TABLE V-3

(continued)

Plant Code	SILVER RECOVERY			BLEACH REGENERATION					DEVELOPER		WASH WATER SILVER RECOVERY
		METHODS			METHODS						
	Usage	Primary	Tailing	Usage	Ferri-cyanide	EDTA	Chromate	Bleach-Fix	Coupler Recovery	Regener-ation	Method
4229	All	B	B	NA					NA	X	None
4550	All	A,B	B	All	D	F	NA	F	H	X	None
4666	All	A,B	B	All	D	NA	NA	NA	H	X	None
4849	All	A,B	None	Partial	X,D	NA	G	F	NA	G	None
5120	All	A,B	NG	All	NA	F	NA	F	NA	X	None
5359	All	B	A	NA					NA	X	None
5552	All	A,B	B	All	D	NA	NA	NA	H	X	None
6174	All	A,B	A	All	D	G	NA	F	NA	X	None
6208	All	B,B In-Line	B,C	Partial	D	NA	X	NA	NA	G	C
6237	All	A,B	None	Partial	X,D	G	NA	X,F	I	X	None
6443	All	A,B	B	All	D	F	NA	F	NA	X	None
6582	All	A,B	A	All	D	G	NA	F	NA	X	None
6726	All	A,B	B	All	D	NA	NA	NA	H	X	None
7644	Partial	B	None	None	NA	X	NA	X	NA	X	None
7781	All	B	A	All	NA	G	NA	F	NA	X	J,K
8058	All	A	None	All	NA	G	NA	F	NA	X	None
8226	All	A	None	All	D	NA	G	NA	NA	X	None
9061	All	B,B In-Line	B	All	D	NA	G	NA	NA	X	C
9297	All	B,B In-Line	B	All	E	NA	NA	F	NA	X	None
9942	All	A	None	Partial	X	F	NA	F	NA	X	None

KEY:

A - Metallic Replacement
B - Electrolytic
C - Resin Ion Exchange
D - Persulfate
E - Ozone
F - Aeration and Chemical Addition
G - Chemical Addition
H - Acidify with Sodium Bisulfate
I - Acidify with Carbon Dioxide
J - Reverse Osmosis
K - Precipitation and Settling
NA - Not Applicable
X - Used and Not Regenerated
Y - Off-Site Recovery
NG - Not Given

TABLE V-3
(continued)

Plant	Use of Silver Recovery on Fix Solutions		Regeneration of Bleaches	
	Usage	Method	Ferricyanide Bleach	Other Bleaches
0201	All	A	No	Yes
0202	All	A,B	NA	Yes
0203	All	B	NA	Yes
0204	Partial	A	No	Partial
0205	Partial	B	No	NG
0206	All,NIS	A,B	NA	Yes
0207	All	A	NA	Yes
0208	All	A	Yes	Yes
0209	Partial	A	NA	Partial
0210	All	A	No	Yes
0211	All	A,B	NA	Yes
0212	All	A	NA	No
0213	All	B	No,NIS	Yes
0214	All	A	NA	NG
0215	All	A	Yes	Yes
0216	All	A	NA	No,NIS
0217	All	A,B	Partial	Yes
0218	Partial	A,B	No	Yes
0219	All	A	No,NIS	Yes
0220	All	A	NA	Yes
0221	All	B	NA	No
0222	All	A	No	Yes
0223	Partial	A,B	Yes	Partial
0224	All	A	NA	Yes
0225	All	A	NA	Yes
0226	All	A,B	NA	Yes
0227	Partial	B	Partial	No
0228	Partial	B	Partial	No
0229	Partial	C	No	NG
0230	Partial	A	No,NIS	Partial
0231	All	B	Partial	No
0232-0237	All,NIS	B	Yes	Yes

KEY:
A - Metallic Replacement
B - Electrolytic
C - Off-site

NA - Not Applicable
NG - Information Not Given
NIS- Waste Not Included in Sample

to the process. The waste fix has gone through primary and tailing silver recovery prior to mixing with the wash water. The silver is recovered from the resin on site by backwashing the resin with a proprietary concentrate. Plant 7781 treats the wash water with a reverse osmosis (RO) system and removes the silver from the concentrate by sulfide precipitation and settling. Before introduction to the RO unit, the wash water is equalized and filtered. Plant 9061 also uses a proprietary resin ion exchange system to recover silver from wash water. The silver is recovered from the resin off site by a contractor and the waste wash water is discharged.

While ferricyanide and ferric EDTA bleach regeneration is not as universally practiced as silver recovery at the plants visited, most plants do some regeneration of bleach. In most cases where a bleach was not regenerated, it was from a little-used process.

Dichromate bleach is not regenerated. Some plants reuse a portion of the bleach overflow by discharging a portion and reconstituting the remainder. Plant 6208 uses a "replenish-on-demand" dichromate bleach replenishment technique which was described in Section III. In addition the plant uses a resin ion exchange system to reduce the chromium level in the after bleach wash water prior to recycle of the water.

WATER USE

Water is used in the photographic processing industry for the following purposes:

(1) Process water: film and paper wash water, solution make-up water, and area and equipment wash water.

(2) Non-process water: Non-contact cooling and heating water, cooling tower (air conditioning), boiler, and sanitary.

The total (process and non-process) water use for the facilities visited in the industry ranges from 13,200 to 2,100,000 liters per day (3,500 to 550,000 gallons per day). It was observed that more than 95 percent of the process water use in each facility is for film and paper washing. Unless otherwise stated, water use throughout this document refers to process water only.

Process Water

Film and Paper Wash Water

The largest single water process use is for the washing of film and paper during various stages of the process. The function of the wash step is to remove no longer needed chemicals included in the emulsion during manufacture, absorbed into the emulsion during processing, or reaction products created during processing.

Solution Make-up Water

The chemicals used to make up processing solutions are generally supplied to the processor in the form of liquid concentrates or powdered chemical formulations. The processor adds water to make up the solutions to working strength. Waterborne wastes are generated when these solutions are discarded after becoming exhausted or when allowed to overflow during replenishment, as is the common practice.

Area and Equipment Wash Water

Water is used for the washing and rinsing of solution mixing utensils, storage tanks, and processing machines and for area washdown.

Non-Process Water

Some facilities use non-contact water for the heating and cooling of process solutions to maintain proper operating temperatures. This water is not process water since it is contained in enclosed water jackets around process tanks and does not come into contact with raw materials or the product. Other non-process water uses include make-up water for cooling towers, boilers, and lawn sprinkling. The volume of water used for these purposes in this industry is small when compared to process water use except in the case of large plants with cooling towers for air conditioning.

Water Usage

Some general information on water use is included in the results of the industry survey and the EPA telephone survey tabulated in Section III. This information is in terms of ranges of total process water use. During the EPA plant visits, estimates of detailed water use information were obtained from the 20 plants visited, and these estimates are presented in Table V-4 along with total process water use for the remainder of the plants studied. The average total process water use for the 70 plants from which data were obtained is 157,000 liters/1,000 sq m (3,850 gal/1,000 sq ft) of material processed.

PROCESS WASTE

Process waste information was obtained from EPA sampling in 1974, 1976 and 1977, the NAPM sampling effort, and plant supplied self-monitoring data. A major portion of the 1977 EPA sampling effort was devoted to the sampling and analyses for toxic pollutants at four of the five plants sampled. Most of the data were obtained from wastewater samples taken after the application of various controls. The 1977 EPA sampling effort also included the sampling of some process solutions before application of controls. These data were obtained to assist in evaluating the effectiveness of various controls. The production normalizing factor used to calculate the cyanide and chromium amounts found in the following tables relates to the area of emulsion processed using ferricyanide bleach or chromium bleach, respectively. In reference to the cyanide values obtained during the NAPM survey, the actual parameter measured was ferri/ferrocyanide. The listed total cyanide value was calculated by NAPM by multiplying the measured value by the stoichiometric ratio of 0.74.

Tables V-5 and V-6 contain pollutant concentration and quantity information, respectively, on various process solutions before any application of controls. These data were obtained from grab samples collected by EPA during the 1977 sampling effort. The solutions selected for sampling were those solutions that the particular plant reconstituted or regenerated for reuse. With these data, estimates can be made as to the impact on an effluent of not reusing these solutions.

TABLE V-4
ESTIMATED WATER USE FOR PLANTS IN THE PHOTOPROCESSING INDUSTRY

Plant Code	Water Intake liters/1,000 sq m (gal/1,000 sq ft)	Solution Make-up liters/1,000 sq m (gal/1,000 sq ft)	Film and Paper Wash liters/1,000 sq m (gal/1,000 sq ft)	Area Wash Down liters/1,000 sq m (gal/1,000 sq ft)	Total Process liters/1,000 sq m (gal/1,000 sq ft)
0021	*	**	**	**	64,000 (1,600)
0045	*	**	**	**	288,000 (7,060)
0118	*	*	*	*	*
0662	*	**	**	**	80,000 (2,000)
1232	84,700 (2,080)	200 (5.0)	82,700 (2,030)	200 (5.0)	83,100 (2,040)
1421	1,670,000 (41,000)	5,700 (140)	505,000 (12,400)	2,200 (55)	513,000 (12,600)
1465	289,000 (7,100)	4,000 (99)	153,000 (3,760)	*	157,000 (3,860)
1635	*	**	**	**	78,000 (1,900)
2146	*	**	**	**	160,000 (3,900)
2387	*	1,000 (25)	101,000 (2,470)	negligible	101,000 (2,490)
2465	*	**	**	**	192,000 (4,700)
2488	*	**	**	**	96,000 (2,400)
2714	21,000 (520)	570 (14)	18,300 (450)	190 (4.6)	19,200 (470)
2892	538,000 (13,200)	**	**	**	**
3075	167,000 (4,100)	530 (13)	161,000 (3,950)	200 (5)	162,000 (3,970)
3437	*	**	**	**	110,000 (2,700)
3455	448,000 (11,000)	7,130 (175)	361,000 (8,870)	3,800 (93)	372,000 (9,140)
3630	*	**	**	**	73,000 (1,800)
4228	*	**	**	**	270,000 (6,600)

---

* Not given

** Not allocated

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TABLE V-4
(continued)

Plant Code	Water Intake liters/1,000 sq m (gal/1,000 sq ft)	Solution Make-up liters/1,000 sq m (gal/1,000 sq ft)	Film and Paper Wash liters/1,000 sq m (gal/1,000 sq ft)	Area Wash Down liters/1,000 sq m (gal/1,000 sq ft)	Total Process liters/1,000 sq m (gal/1,000 sq ft)
4229	192,000 (4,700)	**	**	**	143,000 (3,500)
4550	407,000 (10,000)	4,100 (100)	102,000 (2,500)	*	106,000 (~2,600)
4666	*	**	**	**	207,000 (5,100)
4849	570,000 (14,000)	61,000 (1,500)	497,000 (12,200)	9,400 (230)	570,000 (14,000)
5120	*	**	**	**	57,000 (1,400)
5359	149,000 (3,650)	450 (11)	146,000 (3,580)	94 (2.3)	147,000 (3,600)
5552	*	**	**	**	109,000 (2,700)
6174	*	*	*	*	49,500 (1,200)
6208	103,000 (2,520)	1,400 (34)	98,000 (2,410)	340 (8.4)	100,000 (2,450)
6237	*	1,400 (35)	40,300 (990)	1,400 (35)	43,200 (1,060)
6443	53,800 (1,320)	**	**	**	51,300 (1,260)
6582	*	**	**	**	92,000 (2,300)
6726	*	**	**	**	200,000 (4,900)
7644	135,000 (3,300)	780 (19)	120,000 (2,950)	1,960 (48)	122,000 (3,000)
7781	17,500 (430)	490 (12)	3,600 (89)	4,900 (120)	9,000 (220)
8058	171,000 (4,200)	1,800 (45)	36,300 (890)	negligible	38,300 (940)
8226	*	**	**	**	180,000 (4,400)
9061	619,000 (15,200)	220 (5.5)	530,000 (13,000)	*	530,000 (13,000)
9297	522,000 (12,800)	10,600 (260)	281,000 (6,900)	*	293,000 (~7,200)
9942	*	*	*	*	*

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* Not given

** Not allocated

TABLE V-4
(continued)

Plant Code	Total Process Water 1/1,000 sq m (gal/1,000 sq ft)	Plant Code	Total Process Water 1/1,000 sq m (gal/1,000 sq ft)
0201	188,000 (4,610)	0220	167,000 (4,090)
0202	171,000 (4,200)	0221	63,200 (1,550)
0203	291,000 (7,140)	0222	155,000 (3,800)
0204	111,000 (2,720)	0223	28,600 (700)
0205	258,000 (6,340)	0224	62,000 (1,520)
0206	165,000 (4,050)	0225	137,000 (3,360)
0207	46,400 (1,140)	0226	106,000 (2,600)
0208	105,000 (2,580)	0227	259,000 (6,350)
0209	288,000 (7,060)	0228	28,100 (690)
0210	110,000 (2,710)	0229	NA
0211	51,900 (1,270)	0230	108,000 (2,650)
0212	3,280,000 (80,500)*	0231	83,800 (2,060)
0213	109,000 (2,670)	0232	280,000 (6,880)
0214	137,000 (3,370)	0233	193,000 (4,740)
0215	205,000 (5,040)	0234	419,000 (10,300)
0216	13,900,000 (342,000)*	0235	201,000 (4,940)
0217	44,800 (1,100)	0236	141,000 (3,460)
0218	96,800 (2,380)	0237	252,000 (6,180)
0219	50,600 (1,240)		

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* Not included in overall average. Plants indicated values not representative of normal water use.

NA Total water intake not allocated to process water and non-process use.

TABLE V-4
(continued)

Plant Code	Sanitary liters/1,000 sq m (gal/1,000 sq ft)	Non-Contact Heating and Cooling liters/1,000 sq m (gal/1,000 sq ft)	Other Non-Process liters/1,000 sq m (gal/1,000 sq ft)	Total Non-Process liters/1,000 sq m (gal/1,000 sq ft)
0021	*	*	*	*
0045	*	*	*	*
0118	*	*	*	*
0662	*	*	*	*
1232	1,800 (45)	None	None	1,800 (45)
1421	334,000 (8,200)	672,000 (16,500)	*	*
1465	3,000 (74)	None	129,000 (3,170)	132,000 (3,240)
1635	*	*	*	*
2146	*	*	*	*
2387	2,500 (62)	None	*	*
2465	*	*	*	*
2488	*	*	*	*
2714	2,200 (55)	None	None	2,200 (55)
2892	*	*	*	*
3075	5,300 (130)	None	None	5,300 (130)
3437	*	*	*	*
3455	7,130 (175)	67,600 (1,660)	*	*
3630	*	*	*	*
4228	*	*	*	*

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* Not given

** Not allocated

TABLE V-4
(continued)

Plant Code	Sanitary liters/1,000 sq m (gal/1,000 sq ft)	Non-Contact Heating and Cooling liters/1,000 sq m (gal/1,000 sq ft)	Other Non-Process liters/1,000 sq m (gal/1,000 sq ft)	Total Non-Process liters/1,000 sq m (gal/1,000 sq ft)
4229	49,000 (1,200)	None	None	48,900 (1,200)
4550	8,600 (210)	85,600 (2,100)	25,300 (620)	118,000 (2,900)
4666	*	*	*	*
4849	*	*	*	*
5120	*	*	*	*
5359	1,700 (42)	None	450 (11)	2,200 (53)
5552	*	*	*	*
6174	*	*	*	*
6208	2,000 (50)	None	700 (17)	2,700 (67)
6237	*	*	*	*
6443	*	*	*	*
6582	*	*	*	*
6726	*	*	*	*
7644	13,800 (340)	None	None	13,800 (340)
7781	4,500 (110)	3,600 (89)	130 (3.2)	8,100 (200)
8058	14,700 (360)	None	120,000 (2,950)	134,000 (3,300)
8226	*	*	*	*
9061	4,500 (110)	84,700 (2,080)	220 (5.5)	89,200 (2,190)
9297	**	**	**	288,000 (5,600)
9942	*	*	*	*

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* Not given

** Not allocated

Table V-7 contains data obtained from grab samples taken before and after various silver recovery operations. These samples were taken during the 1977 EPA sampling effort.

Tables V-8 and V-9 contain pollutant concentration and quantity information, respectively, on the effluent from plants using in-process controls for silver recovery, coupler recovery, and bleach regeneration where applicable. A description of the in-process controls used at the plants was previously given in Table V-3. The hydraulic load values given in Table V-9 may not always agree with the process water values for a specific plant given in Table V-4. The process water information in Table V-4 represents estimates or long-term averages in most cases while the water data in Table V-9 generally represent a measured flow over a relatively short sampling period.

EFFLUENT CHARACTERISTICS

The results in this section describe plant effluents after the application of various end-of-pipe treatments. These treatments are in addition to the various controls which were previously described.

End-of-pipe treatment information for plants using such treatments is given in Table V-10. Table V-11 contains before- and after-treatment data for some individual treatment operations. Tables V-12 and V-13 contain the plant effluent data for plants using in-process controls plus end-of-pipe treatments, pollutant concentrations, and amounts, respectively.

TABLE V-5

PROCESSING MACHINE TANK OVERFLOW COMPOSITION WITHOUT APPLICATION OF IN-PROCESS CONTROLS - POLLUTANT CONCENTRATION

Plant Code	Stream Description	Sampling Date	Pollutant Concentration, mg/liter										
			Cyanide	TOC	Cadmium	Chromium	Silver	BOD	Nitrogen-Ammonia	Iron	Lead	TSS	TDS
2714	Ferricyanide Bleach	Aug 77	15,800	13,000	<0.02	4.2	4.1	--	--	5,562	0.22	30	128,000
	EDTA Bleach	Aug 77	--	43,600	<0.02	2.0	268	--	--	16,282	<0.02	62	253,000
	Bleach-Fix	Aug 77	--	45,500	<0.02	0.6	2,109	--	--	4,884	0.5	112	205,000
4550	Ferricyanide Bleach	Jul 77	50,200	30,750	0.40	1.3	8	<10,000	3,089	11,118	2.0	101	304,750
	EDTA Bleach	Jul 77	3.1	42,150	0.4	12	233	8,290	64,000	12,102	2.0	112	227,600
	Bleach-Fix (R-5)	Jul 77	0.70	33,900	<0.6	5.7	2,025	13,300	38,000	7,718	1.0	56	195,400
	Bleach-Fix (EP-2)	Jul 77	1.1	47,150	1.0	6	1,582	28,000	30,000	8,023	1.4	82	209,400
6208	Color Developer	Aug 77	--	6,450	0.34	0.09	1.4	--	--	2.9	0.25	9.3	40,400
	Ferricyanide Bleach	Aug 77	14,750	8,300	<0.02	0.09	0.38	--	--	7,560	0.42	24	98,800
	Dichromate Bleach	Aug 77	--	395	0.68	2,194	0.65	--	--	0.70	<0.02	12	58,200
7781	Color Developer (A)	Aug 77	--	15,000	86	0.10	1.5	--	--	2.4	7.5	18	78,400
	Color Developer (B)	Aug 77	--	16,700	1.1	0.26	0.49	--	--	3.7	0.09	10	52,600
	EDTA Bleach	Aug 77	--	23,200	0.09	3.6	36	--	--	7,722	0.14	86	206,800
	Bleach-Fix (A)	Aug 77	--	41,600	80	1.3	4,356	--	--	5,310	22	124	292,000
	Bleach-Fix (B)	Aug 77	--	50,750	0.24	2.9	2,111	--	--	13,236	0.7	51	306,200

TABLE V-6

PROCESSING MACHINE TANK OVERFLOW COMPOSITION WITHOUT APPLICATION OF IN-PROCESS CONTROLS - POLLUTANT AMOUNT

Plant Code	Stream Description	Hydraulic Load, liters/sq m	(gal/1,000 sq ft)	Pollutant Quantity, kg/1,000 sq m (lb/1,000 sq ft) Cyanide	Cadmium	Chromium	Silver
2714	Ferricyanide Bleach	2,800	(69)	44 (9.1)	$<5.6 \times 10^{-5}$ $(<1.1 \times 10^{-5})$	1.2×10^{-2} (2.4×10^{-3})	1.15×10^{-2} (2.35×10^{-3})
	EDTA Bleach	570	(14)	--	$<1.1 \times 10^{-5}$ $(<2.3 \times 10^{-6})$	1.1×10^{-3} (2.3×10^{-4})	0.15 (0.03)
	Bleach-Fix	290	(7.1)	--	$<5.8 \times 10^{-6}$ $(<1.2 \times 10^{-6})$	1.7×10^{-4} (3.6×10^{-5})	0.61 (0.12)
4550	Ferricyanide Bleach	810	(20)	40.9 (8.38)	3.3×10^{-4} (6.7×10^{-5})	1.5×10^{-3} (2.2×10^{-4})	6.5×10^{-3} (1.3×10^{-3})
	EDTA Bleach	1,700	(42)	0.0054 (0.0011)	6.8×10^{-4} (1.4×10^{-4})	2.0×10^{-2} (4.2×10^{-3})	0.40 (0.08)
	Bleach-Fix (R-5)	610	(15)	4.3×10^{-4} (8.8×10^{-5})	$<3.7 \times 10^{-4}$ $(<7.5 \times 10^{-5})$	3.5×10^{-3} (7.1×10^{-4})	1.24 (0.25)
	Bleach-Fix (EP-2)	320	(7.9)	3.5×10^{-4} (7.2×10^{-5})	3.2×10^{-4} (6.6×10^{-5})	1.9×10^{-3} (3.9×10^{-4})	0.51 (0.10)
6208	Color Developer	660	(16.2)	--	2.24×10^{-4} (4.59×10^{-5})	6.0×10^{-5} (1.2×10^{-5})	9.2×10^{-4} (1.9×10^{-4})
	Ferricyanide Bleach	190	(4.75)	2.9 (0.59)	$<3.8 \times 10^{-6}$ $(<7.8 \times 10^{-7})$	1.7×10^{-5} (3.6×10^{-6})	7.2×10^{-5} (1.5×10^{-5})
	Dichromate Bleach	120	(2.86)	--	7.9×10^{-5} (1.6×10^{-5})	0.26 (0.05)	7.8×10^{-5} (1.6×10^{-5})
7781	Color Developer	200	(5.0)	--	1.7×10^{-2} (3.5×10^{-3})	2.0×10^{-5} (4.1×10^{-6})	3.0×10^{-4} (6.1×10^{-5})
	Color Developer	330	(8.0)	--	3.6×10^{-4} (7.3×10^{-5})	8.6×10^{-5} $1.8 \times 10^{-5})$	1.6×10^{-4} (3.3×10^{-5})
	EDTA Bleach	210	(5.1)	--	1.9×10^{-5} (3.9×10^{-6})	7.6×10^{-4} (1.6×10^{-4})	7.6×10^{-2} (1.6×10^{-2})
	Bleach-Fix	310	(7.7)	--	2.5×10^{-2} (5.1×10^{-3})	4.0×10^{-4} (8.2×10^{-5})	1.35 (0.28)
	Bleach-Fix	330	(8.0)	--	7.9×10^{-5} (1.6×10^{-5})	9.6×10^{-4} (2.0×10^{-4})	0.70 (0.14)

TABLE V-6

(continued)

Plant Code	Stream Description	Pollutant Quantity, kg/1,000 sq m (lb/1,000 sq ft)						
		TOC	BOD	Nitrogen-Ammonia	Iron	Lead	TSS	TDS
2714	Ferricyanide Bleach	37 (7.5)	--	--	15.6 (3.2)	6.2×10^{-4} (1.3×10^{-4})	0.083 (0.017)	360 (74)
	EDTA Bleach	25 (5.1)	--	--	9.2 (1.9)	$<1.1 \times 10^{-5}$ ($<2.3 \times 10^{-6}$)	0.035 (0.0072)	150 (30)
	Bleach-Fix	13 (2.7)	--	--	1.4 (0.3)	1.5×10^{-4} (3.0×10^{-5})	0.032 (0.0066)	59 (12)
4550	Ferricyanide Bleach	25.0 (5.13)	<8.2 (1.7)	2.5 (0.52)	9.0 (1.8)	1.6 (0.3)	0.083 (0.017)	250 (51)
	EDTA Bleach	72.3 (14.8)	14.2 (2.91)	110 (22)	20.6 (4.2)	3.4×10^{-3} (7.0×10^{-4})	0.19 (0.039)	390 (80)
	Bleach-Fix (R-5)	20.7 (4.24)	8.11 (1.66)	23 (4.8)	4.7 (0.96)	6.1×10^{-4} (1.2×10^{-4})	0.034 (0.0070)	120 (24)
	Bleach-Fix (EP-2)	15.2 (3.11)	9.01 (1.85)	9.8 (2.0)	2.6 (0.5)	4.5×10^{-4} (9.2×10^{-5})	0.026 (0.0054)	68 (14)
6208	Color Developer	4.26 (0.872)	--	--	1.9×10^{-3} (3.9×10^{-4})	1.65×10^{-4} (3.38×10^{-5})	0.0064 (0.0013)	27 (5.5)
	Ferricyanide Bleach	1.6 (0.33)	--	--	1.44 (0.29)	8.0×10^{-5} (1.6×10^{-5})	0.0049 (0.0010)	19 (3.9)
	Dichromate Bleach	0.046 (0.0094)	--	--	8.4×10^{-5} (1.7×10^{-5})	$<2.4 \times 10^{-6}$ ($<4.9 \times 10^{-7}$)	0.0014 (0.00029)	6.8 (1.4)
7781	Color Developer (A)	3.06 (0.626)	--	--	4.8×10^{-4} (9.8×10^{-5})	1.5×10^{-3} (3.1×10^{-4})	3.6×10^{-3} (7.5×10^{-4})	16 (3.3)
	Color Developer (B)	5.51 (1.13)	--	--	1.2×10^{-3} (2.5×10^{-4})	3.0×10^{-5} (6.1×10^{-6})	3.3×10^{-3} (6.7×10^{-4})	17 (3.5)
	EDTA Bleach	4.61 (0.945)	--	--	1.6 (0.3)	2.9×10^{-4} (6.0×10^{-5})	0.018 (0.0037)	43 (8.8)
	Bleach-Fix (A)	13.0 (2.67)	--	--	1.65 (0.34)	6.8×10^{-2} (1.4×10^{-2})	0.039 0.0080	78 (16)
	Bleach-Fix (B)	16.5 (3.39)	--	--	4.4 (0.9)	2.3×10^{-4} (4.7×10^{-5})	0.017 (0.0034)	98 (20)

TABLE V-7

BEFORE AND AFTER RESULTS OF VARIOUS SILVER RECOVERY OPERATIONS

Plant Code	Sampled Stream Description	Control Type	Date	Pollutant Concentration, mg/liter										
				Cyanide	TOC	Cadmium	Chromium	Silver	BOD	Phenols	Iron	Lead	TSS	TDS
4550	Bleach-fix (EP-2) before SR	Silver recovery	7-77	1.1	47,150	1.0	7.0	1,500	28,000	0.04	86,960	1.33	82	209,400
	Bleach-fix (EP-2) after SR	Silver recovery	--	--	--	--	--	4.7	--	--	--	--	--	--
6208	Influent to ion exchange	SR from wash water and recycle	8-77	0.02	29	0.017	0.21	2.0	--	0.15	0.10	<0.05	14.1	1,000
	Ion exchange effluent			0.01	25	0.013	0.10	0.14	--	0.03	0.09	<0.05	3.5	973
7781	Influent to RO	Wash water recycle	8-77	--	153	0.017	0.04	68	--	0.73	39	0.19	103	1,210
	RO permeate			--	635	0.25	<0.02	14	--	18.3	26	0.08	<1	3,060
	RO concentrate (influent to metals removed)	SR and end-of-pipe treatment for		--	3,710	4.9	0.72	57	--	11.3	340	1.8	34	26,480
	Metals removal effluent - partial influent to aeration	reduction of heavy metals		--	3,450	0.06	0.16	0.08	--	4.9	5.8	0.07	19.4	53,100
9061	Influent to ion exchange no. 1	SR from wash water and recycle	8-77	0.32	37	0.013	0.26	0.74	--	<0.02	0.92	0.04	10.2	853
	Ion exchange effluent no. 1			0.03	<5	<0.02	0.02	0.04	--	<0.02	0.20	<0.05	2.5	586
	Influent to ion exchange no. 2			<0.01	21	0.02	0.06	0.60	--	<0.02	0.18	<0.05	5.5	695
	Ion exchange effluent no. 2			<0.01	4.4	0.013	0.04	0.10	--	<0.02	0.19	<0.05	11.8	690

TABLE V-8

EFFLUENT CHARACTERISTICS WITH APPLICATION OF CONTROLS - CONCENTRATION

Plant Code	Sample Information			Pollutant Concentration, mg/liter										
	Description	Date	By	Cyanide	TOC	Cadmium	Chromium	Silver	BOD	Nitrogen-Ammonia	Iron	Lead	TSS	TDS
0021	Avg. of 3 24-hr. composites[4]	1977	Self	0.18	--	--	--	2.4	507	--	--	--	--	1,002
0045	See Table V-12													
0118	Avg. of 1 to 3 8-hr. FP composites	75-76	Self	4.0	--	<0.01	0.60	0.20	96	--	--	<0.09	14	681
0662	Single 24-hr. composite[4]	4-77	Self	1.09	--	--	--	1.5	497	--	--	--	--	662
1232	Not available													
1330	Avg. of 5 daily FP composites	1-76	Self	0.001	--	0.001	0.005	0.71	--	--	--	0.0009	14	--
1421	Avg. of 10 monthly samples	76-77	Self	--	--	--	--	0.20	30	5.5	2.90	--	8	--
1465	See Table V-12													
1635	Avg. of 3 24-hr. composites[4]	1977	Self	0.30	--	--	--	3.3	326	--	--	--	--	1,184
2146	Single 24-hr. FP composite	12-76	Self	5.6	--	--	<0.005	2.0	245	--	--	--	4	--
2387	Not available													
2465	Single 24-hr. FP composite[5]	9-76	Self	4.2	--	<0.02	0.07	0.46	300	--	4	<0.02	60	1,860
2488	Single 24-hr. FP composite[5]	7-76	Self	3.8	--	<0.02	0.23	0.33	240	--	0.18	0.04	115	1,950
2488	Single 13.5-hr. FP composite[5]	9-76	EPA	7.5	--	<0.02	0.02	0.37	85	7.05	4.2	--	64	--
2714	See Table V-12													
2892	Not available													
3075	Not available													
3437	Avg. of 2 24-hr. composites[5]	1976	Self	2.4	--	<0.02	0.07	0.26	229	--	1.3	<0.02	6.4	1,187
3455	Not available													
3630	Avg. of 4 24-hr. composites[4]	1977	Self	1.1	--	--	--	0.59	76	--	--	--	--	519
4228	Avg. of 2 24-hr. FP composites[5]	1976	Self	8.0	--	<0.02	0.03	0.50	140	--	3.7	<0.03	48	1,610

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[1] FP - flow proportioned.
[2] Plant has divided process wastewaters into two or more outfalls. Pollutants summed in proportion to stream flow.
[3] Represents only portion of total plant discharge of process water.
[4] Discharge does not include ferricyanide bleach waste which is contractor hauled.
[5] Plant batch treats waste fix by precipitation for reduction of cyanide. Treated waste fix not in sample.

TABLE V-8
(continued)

Plant Code	Sample Information: Description	Date	By	Pollutant Concentration, mg/liter: Cyanide	TOC	Cadmium	Chromium	Silver	BOD	Nitrogen-Ammonia	Iron	Lead	TSS	TDS
4229	Not available													
4550	Avg. of 3 24-hr. FP Composites	7-77	EPA	0.4	109	0.01	0.10	0.33	175	9.3	5.9	0.04	25	1,950
4550	Single 24-hr. FP Composite[5]	7-76	Self	0.7	--	<0.02	0.23	0.26	<70	--	23	0.03	15	1,790
4666	Avg.of 4 24-hr. FP Composites[5]	1976	Self	8.1	--	<0.02	0.04	0.33	484	--	4.3	<0.03	29	2,056
4849	Not available													
5120	Single Grab[2]	12-77	Self	0.30[3]	--	0.007[3]	0.0017	0.023	8[3]	--	--	--	<0.5[3]	423[3]
5359	Not available													
5552	Single 24-hr. Composite[5]	8-76	Self	10	--	<0.02	0.07	0.55	165	--	4.2	<0.02	108	1,900
6174	Avg. of 8 24-hr. Composites[4]	76-77	Self	0.67	--	--	--	1.06	506	--	--	--	--	1,086
6208	Avg. of 6 24-hr. FP Composites	1977	Self	0.45	--	--	3.2	0.17	90	--	0.41	--	12	--
6208	Avg. of 3 24-hr. FP Composites	8-77	EPA	0.01	44	0.019	2.8	0.47	78	13	0.19	<0.05	22.4	1,245
6237	Not available													
6443	Single 24-hr. FP[1] Composite	9-76	EPA	0.73	286	<0.02	0.08	3.24	237	69	36.5	--	42	--
6582	Avg. of 3 24-hr. Composites[4]	1977	Self	0.95	--	--	--	1.38	132	--	--	--	--	904
6726	Single 24-hr. Composite[5]	7-76	Self	3.5	--	<0.02	0.08	0.82	165	--	1.52	<0.02	9	780
7644	Not available													
7781	See Table V-12													
8058	Not available													
8226	Single 24-hr. FP Composite	3-76	Self	0.54	--	--	0.75	0.3	209	--	--	--	88	--
9061	Not available													
9297	Not available													
9942	Avg. of 1 to 3 8-hr. FP Composites	75-76	Self	3.99	--	<0.01	<0.01	0.29	28	--	--	<0.02	5.4	369

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[1] FP - flow proportioned.
[2] Plant has divided process wastewaters into two or more outfalls. Pollutants summed in proportion to stream flow.
[3] Represents only portion of total plant discharge of process water.
[4] Discharge does not include ferricyanide bleach waste which is contractor hauled.
[5] Plant batch treats waste fix by precipitation for reduction of cyanide. Treated waste fix not in sample.

TABLE V-8

EFFLUENT CHARACTERISTICS WITH APPLICATION OF CONTROLS - CONCENTRATIONS
(continued)

Plant Code	POLLUTANT CONCENTRATION mg/liter			
	BOD	COD	Ag	Total CN
0201	156	288	0.77	7.8
0202	204	516	0.87	
0203	61.2	192	0.89	
0204	228	588	5.0	2.7
0205	431	876	3.5	53
0206	180	384	0.48	
0207	336	1,190	16.8	
0208	336	1,920	12.0	
0209	63.5	312	1.8	
0210	168	312	0.77	2.1
0211	168	480	2.64	
0212	40.7	180	0.25	
0213	132	276	1.9	10.8
0214	312	576	2.4	
0215	132	408	4.2	0.4
0216	10.1	34.8	4.5	
0217	395	936	5.8	1.4
0218	264	876	1.1	3.4
0219	192	804	2.6	0.8
0220	98.3	360	2.9	
0221	44.3	288	5.4	
0222	132	480	0.76	

TABLE V-8

EFFLUENT CHARACTERISTICS WITH APPLICATION OF CONTROLS - CONCENTRATIONS (continued)

Plant Code	POLLUTANT CONCENTRATION mg/liter			
	BOD	COD	Ag	Total CN
0223	527	288	7.7	0.6
0224	252	624	1.0	
0225	204	576	1.8	
0226	192	552	2.0	
0227	240	444	2.5	1.6
0228	76.7	300	1.7	4.6
0229	55.1	144	1.0	2.1
0230	348	936	7.2	
0231	56.3	276	0.52	
0232	372	708	4.7	4.5
0233	228	636	0.25	3.1
0234	156	312	0.14	6.2
0235	204	1,040	0.94	6.8
0236	75.5	276	0.62	4.2
0237	168	1,200	0.56	5.4

TABLE V-9

EFFLUENT CHARACTERISTICS WITH APPLICATION OF CONTROLS - POLLUTANT AMOUNTS

Plant Code	See Note	Sampled By	Hydraulic Load, liters/1,000 sq m (gal/1,000 sq ft)	Pollutant Amount, kg/1,000 sq m (lb/1,000 sq ft)			
				Cyanide	Cadmium	Chromium	Silver
0021	2, 3	Self	64,000 (1,580)	--	--	--	0.16 (0.032)
0045	See Table V-13						
0118	No production information						
0662	2, 3	Self	80,300 (1,970)	--	--	--	0.12 (0.025)
1232	Not available						
1330	No production information						
1421		Self	1,300,000 (33,000)	--	--	--	0.27 (0.055)
1465	See Table V-13						
1635	2, 3	Self	77,800 (1,910)	--	--	--	0.25 (0.052)
2146		Self	161,000 (3,960)	--	--	--	0.32 (0.066)
2387	Not available						
2465	4	Self	192,000 (4,720)	1.0 (0.21)	<0.0039 (8 x 10^{-})	--	0.088 (0.018)
2488	4	Self	96,100 (2,360)	0.4 (0.08)	<0.002 (4 x 10^{-})	--	0.032 (0.0065)
2488	4	EPA	478,000 (11,740)	0.4 (0.08	<0.0098 (0.002)	--	0.18 (0.036)
2714	See Table V-13						
2892	Not available						
3075	Not available						
3437	4	Self	111,000 (2,730)	0.26 (0.054)	<0.0024 (5 x 10^{-})	--	0.028 (0.0058)
3455	Not available						
3630	2, 3	Self	73,000 (1,800)	--	--	--	0.043 (0.0089)
4228	4	Self	271,000 (6,660)	1.4 (0.28)	<0.0049 (0.001)	--	0.14 (0.028)

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[1] Plant has divided process waste into two or more outfalls. Pollutants summed in proportion to stream flow.
[2] Represents only portion of total plant discharge of process water.
[3] Discharge does not include ferricyanide bleach waste which is contractor hauled.
[4] Plant batch treats waste fix by precipitation for reduction of cyanide. Treated waste fix is not in sample.
[5] Plant uses end-of-pipe treatments on portion of process wastewaters.

TABLE V-9

(continued)

Plant Code	See Note	Sampled By	Hydraulic Load, liters/1,000 sq m (gal/1,000 sq ft)	Pollutant Amount, kg/1,000 sq m (lb/1,000 sq ft)			
				Cyanide	Cadmium	Chromium	Silver
4229	Not available						
4550	1	EPA	221,000 (5,425)	0.32 (0.065)	0.0029 (6×10^{-4})	--	0.073 (0.015)
4550	4	Self	342,000 (8,400)	0.54 (0.11)	<0.0049 (0.001)	--	0.088 (0.018)
4666	4	Self	207,000 (4,070)	1.7 (0.34)	<0.0039 (8×10^{-4})	--	0.068 (0.014)
4849	Not available						
5120	1	Self	57,000 (1,400)	--	2.8×10^{-4} (5.7×10^{-5}) 2	--	0.0013 (2.6×10^{-4})
5359	Not available						
5552	4	Self	109,000 (2,670)	1.9 (0.39)	<0.002 (4×10^{-4})	--	0.059 (0.012)
6174	3	Self	49,700 (1,220)	1.0 (0.21)	--	--	0.054 (0.011)
6208		Self	138,000 (3,400)	1.2 (0.24)	--	0.49 (0.10)	0.024 (0.0050)
6208		EPA	102,000 (2,500)	0.014 (0.0028)	0.0020 (4.0×10^{-4})	0.32 (0.066)	0.048 (0.0098)
6237	Not available						
6443		EPA	51,300 (1,260)	0.039 (0.008)	<0.001 (2.1×10^{-4})	0.005 (0.001)	0.17 (0.034)
6582	2, 3	Self	92,100 (2,260)	--	--	--	0.13 (0.026)
6726	4	Self	200,000 (4,900)	0.76 (0.16)	<0.0039 (8×10^{-4})	--	0.17 (0.034)
7644	Not available						
7781	See Table V-13						
8058	Not available						
8226		Self	176,000 (4,320)	0.63 (0.13)	--	0.16 (0.033)	0.054 (0.011)
9061	Not available						
9297	Not available						
9942	No production information						

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[1] Plant has divided process waste into two or more outfalls. Pollutants summed in proportion to stream flow.
[2] Represents only portion of total plant discharge of process water.
[3] Discharge does not include ferricyanide bleach waste which is contractor hauled.
[4] Plant batch treats waste fix by precipitation for reduction of cyanide. Treated waste fix is not in sample.
[5] Plant uses end-of-pipe treatments on portion of process wastewaters.

TABLE V-9
(continued)

Plant Code	Pollutant Amount, kg/1,000 sq m (lb/1,000 sq ft)						
	TOC	BOD	Nitrogen-Ammonia	Iron	Lead	TSS	TDS
0021	--	32.7 (6.7)	--	--	--	--	64.5 (13.2)
0045	See Table V-13						
0118	No production information						
0662	--	40.0 (8.2)	--	--	--	--	53.2 (10.9)
1232	Not available						
1330	No production information						
1421	--	40.0 (8.2)	7.32 (1.5)	3.91 (0.80)	--	10.7 (2.2)	--
1465	See Table V-13						
1635	--	25.4 (5.2)	--	--	--	--	92.3 (18.9)
2146	--	39.5 (8.1)	--	--	--	0.63 (0.13)	--
2387	Not available						
2465	--	58.6 (12)	--	0.78 (0.16)	<0.0039 (8×10^{-4})	11.7 (2.4)	357.4 (73.2)
2488	--	40.5 (8.3)	3.37 (0.69)	2.00 (0.41)	--	30.8 (6.3)	--
2488	--	22.9 (4.7)	--	0.017 (0.0035)	0.0039 (8×10^{-4})	11.2 (2.3)	187.5 (38.4)
2714	See Table V-13						
2892	Not available						
3075	Not available						
3437	--	25.4 (5.2)	--	0.15 (0.030)	<0.0024 (5×10^{-4})	0.68 (0.14)	131.8 (27.0)
3455	Not available						
3630	--	5.37 (1.1)	--	--	--	--	38.1 (7.8)
4228	--	38.1 (7.8)	--	0.98 (0.20)	<0.0098 (0.002)	12.7 (2.6)	436.0 (89.3)

TABLE V-9
(continued)

Plant	Pollutant Amount, kg/1,000 sq m (lb/1,000 sq ft)						
Code	TOC	BOD	Nitrogen-Ammonia	Iron	Lead	TSS	TDS
4229	Not available						
4550	23.9 (4.9)	38.6 (7.9)	2.05 (0.42)	1.32 (0.27)	0.0098 (0.002)	5.4 (1.1)	430.6 (88.2)
4550	--	<23.9 (4.9)	--	7.81 (1.6)	0.0098 (0.002)	5.4 (1.1)	612.8 (125.5)
4666	--	97.7 (20)	--	0.88 (0.18)	<0.0049 (0.001)	5.86 (1.2)	424.8 (87.0)
4849	Not available						
5120	--	0.024 $(0.07)^2$	--	--	--	7.8 x 10^{-5} $(0.004)^2$	59.8 $(3.5)^2$
5359	Not available						
5552	--	1.81 (4.7)	--	0.46 (0.094)	<0.002 (4 x 10^{-4})	11.7 (2.4)	206.5 (42.3)
6174	--	24.9 (5.1)	--	--	--	--	43.0 (8.8)
6208	--	12.7 (2.6)	--	0.059 (0.012)	--	1.66 (0.34)	--
6208	4.4 (0.91)	7.81 (1.6)	1.32 (0.27)	0.019 (0.0039)	<0.0049 (0.001)	2.29 (0.47)	126.5 (25.9)
6237	Not available						
6443	15 (3.0)	12 (2.5)	3.6 (0.73)	1.9 (0.38)	--	2.1 (0.44)	--
6582	--	12.2 (2.5)	--	--	--	--	83.5 (17.1)
6726	--	32.7 (6.7)	--	0.30 (0.062)	<0.0031 (8 x 10^{-4})	1.81 (0.37)	155.8 (31.3)
7644	Not available						
7781	See Table V-13						
8058	Not available						
8226	--	36.6 (7.5)	--	--	--	15.6 (3.2)	--
9061	Not available						
9297	Not available						
9942	No production information						

TABLE V-9

(continued)

Plant Code	Hydraulic Load, liters/1,000 sq m (gal/1,000 sq ft)		Pollutant Amount, kg/1,000 sq m (lb/1,000 sq ft)			
			BOD	COD	Ag	Total CN
0201	160,000	(3,930)	24.9(5.1)	46.4(9.5)	0.12(0.025)	8.3 (1.7)
0202	189,000	(4,640)	38.6(7.9)	98.1(20.1)	0.17(0.034)	
0203	246,000	(6,030)	15.1(3.1)	47.8(9.8)	0.22(0.045)	
0204	93,500	(2,300)	21.5(4.4)	55.2(11.3)	0.47(0.096)	23(4.8)
0205	290,000	(7,120)	126.5(25.9)	250.4(51.7)	1.03(0.21)	48(9,8)
0206	120,000	(2,960)	21.5(4.4)	46.4(9.5)	0.059(0.012)	
0207	50,000	(1,380)	19.0(3.9)	66.9(13.7)	0.98(0.20)	
0208	100,000	(2,450)	33.7(6.9)	199.2(40.8)	1.2(0.25)	
0209	297,000	(7,300)	19.0(3.9)	93.7(19.2)	0.54(0.11)	
0210	115,000	(2,830)	20.0(4.1)	36.6(715)	0.088(0.018)	21(4.3)
0211	63,000	(1,550)	10.3(2.1)	30.3(6.2)	0.17(0.034)	
0212	3,290,000	(80,700)	133.3(27.3)	572.2(117.2)	0.83(0.17)	
0213	114,000	(2,810)	15.1(3.1)	31.7(6.5)	0.21(0.049)	370(75)
0214	156,000	(3,830)	48.8(10.0)	88.9(18.2)	0.037(0.0075)	
0215	161,000	(3.960)	21.5(4.4)	66.4(13.6)	0.68(0.14)	4.4(0.90)
0216	13,900,000	(341,000)	139.2(28.5)	488.7(100.1)	6.3(1.3)	
0217	70,000	(1,720)	27.3(5.6)	65.4(13.4)	0.40(0.082)	5.4(1.1)
0218	129,000	(3.180)	34.2(7.0)	113(23.1)	1.4(0.29)	13(2.6)
0219	32,100	(790)	6.3(1.3)	25.9(5.3)	0.83(0.17)	0.59(0.12)
0220	183,000	(4,500)	18.1(3.7)	65.4(13.4)	0.054(0.011)	
0221	63.100	(1,550)	2.8(0.57)	18.1(3.7)	0.34(0.070)	
0222	151,000	(3,700)	19.5(4.0)	73.2(15.0)	0.68(0.14)	
0223	32,500	(800)	17.1(3.5)	52.7(10.8)	0.25(0.051)	7.3(1.5)
0224	72,400	(1,780)	18.1(3.7)	44.9(9.2)	0.073(0.015)	
0225	83,500	(2,050)	17.1(3.5)	48.3(9.9)	0.15(0.031)	
0226	114,000	(2,800)	21.5(4.4)	62.5(12.8)	0.23(0.048)	
0227	344,000	(8,460)	81.5(16.7)	154.8(31.7)	0.88(0.18)	2.1(0.43)
0228	20,900	(510)	1.6(0.33)	6.35(1.3)	0.034(0.007)	8.3(1.7)
0229	817,000	(200,000)	44.9(9.2)	114.3(23.4)	0.82(0.167)	18(3.6)
0230	111,000	(2,730)	39.1(8.0)	104.0(21.3)	0.80(0.163)	
0231	86,200	(2,120)	4.9(1.0)	23.9(4.9)	0.044(0.009)	
0232	280,000	(6,880)	105.5(21.6)	199.7(40.9)	0.13(0.027)	63(0.26)
0233	193,000	(4,740)	43.0(8.8)	122.1(25.0)	0.049(0.010)	0.59(0.12)
0234	419,000	(10,300)	66.4(13.6)	125.4(26.3)	0.059(0.012)	2.59(0.53)
0235	203,000	(4,980)	40.5(8.3)	211.9(43.4)	0.19(0.039)	1.37(0.28)
0236	141,000	(3,470)	10.7(2.2)	38.5(7.9)	0.088(0.018)	0.59(0.12)
0237	252,000	(6,190)	42.5(8.7)	316.9(64.9)	0.14(0.029)	1.37(0.28)

TABLE V-10

TREATMENT TECHNOLOGIES USED BY PHOTOPROCESSORS SURVEYED

Plant Code	Equalization	Neutralization	Aeration	Ozonation	Flocculation	Precipitation	Clarification	Chlorination	Settling	Filtration	Reverse Osmosis
0045							X				
1465				X (concentrated chemicals only)							
2387									X		
2714	X	X (wash water only)									X
3075									X		
3455	X				X	X	X	X	X	X	
4229	X								X		
4550					X	X (only waste fix containing FeCN)			X		
4849								X (wash water only)			
7781			X	X		X			X	X	X
9297	X		X	X					X		

TABLE V-11

SAMPLING OF IN-PROCESS CONTROLS AND END-OF-PIPE TREATMENTS

Code	Sampled Stream Description	Control Type	Date	Pollutant Concentration, mg/liter										
				Cyanide	TOC	Cadmium	Chromium	Silver	BOD	Phenols	Iron	Lead	TSS	TDS
1465	Influent to Ozonation-(Concentrated chemicals only)	End-of-pipe treatment for reduction of oxygen demand		<0.02	3,700	<0.05	1.35	0.55	4,928	—	228	—	2	17,900
	Ozonation Effluent			<0.02	2,990	<0.05	0.35	0.37	3,232	—	111	—	2	13,900
2714	Influent to RO (paper wash)	End-of-pipe treatment on wash water	8-7	0.04	420	0.017	0.08	6.3	—	<0.01	112	0.09	20	1,895
	RO Permeate (paper wash)			<0.01	178	<0.02	<0.02	0.04	605	0.27	1.79	<0.05	14.5	182
	Influent to RO (film wash)			0.70	24	<0.02	0.022	0.99	—	<0.02	5.1	<0.05	11.8	615
	RO Permeate (film wash)			0.03	6.9	<0.02	0.02	<0.02	7.9	<0.02	0.28	<0.05	9	180
4550	Fix Waste before SR	SR on fix and end-of-pipe treatment for reduction of cyanide	7-77	4,310	—	—	—	576	—	—	—	—	72	87,100
	Influent to Ferro Precipitation (Fix waste after SR)			4,440	—	—	—	21	—	—	—	—	217	92,700
	Ferro Precipitation Effluent			2.0	—	—	—	8.4	—	—	—	—	1,800	119,700
7781	Film Wash (except after fix)-partial influent to aeration	Segregation of wastewater	8-77	—	153	0.017	0.04	1.12	—	0.73	39	0.19	103	1,210
	Influent to RO	Wash water recycle		—	1,100	1.1	<0.05	68	—	17	80	0.27	3.7	5,950
	RO Permeate			—	635	0.25	<0.02	16	—	18.3	26	0.08	<1	3,060
	RO Concentrate (Influent to Metals Removal)	SR and end-of-pipe treatment for reduction of heavy metals		—	3,710	4.9	0.72	57	—	11.3	340	1.8	34	26,480
	Metals Removal Effluent-partial influent to aeration			—	3,450	0.06	0.16	0.08	—	4.9	5.8	0.07	19.4	53,100
	Influent to Ozonation	End-of-pipe treatment		—	2,175	0.04	<0.04	1.2	3,250	7.2	2.5	0.07	253	9,155
	Ozonation Effluent - partial influent to aeration			—	2,400	0.03	<0.03	1.15	3,250	3.21	2.6	0.06	12.2	6,565

TABLE V-12

EFFLUENT CHARACTERISTICS AFTER APPLICATION OF END-OF-PIPE TREATMENTS - POLLUTANT CONCENTRATIONS

Plant Code	Sample Information			Pollutant Concentration, mg/liter										
	Description	Date	By	Cyanide	TOC	Cadmium	Chromium	Silver	BOD	Nitrogen-Ammonia	Iron	Lead	TSS	TDS
0045	Avg. of 3 daily composites	74-76	Self	1.27	--	--	--	1.24	--	--	--	--	--	--
1465	Several values from period[1]	1974	Self	1.4	107	--	--	0.72	155	802[3]	5.1	--	6.4	708
1465	Single 24-hr. Composite[1]	11-74	EPA	0.054	60.8	<0.05	0.05	0.19	57	15	5.5	--	1	471
2714	Avg. of two values[2]	1977	Self	0.2	--	--	--	0.04	9.9	--	--	--	--	216
2714	Grabs from 38,000 liter tanks[1]	8-77	EPA	1.1	672	0.017	0.04	2.7	1,124	350	39.9	0.06	46.5	3,152
7781	Avg. of 3 monthly averages of daily values	1977	Self	--	--	0.20	--	5.6	112	--	17	0.19	41	--
7781	Avg. of 3 24-hr. FP Composites	7-77	EPA	0.04	153	0.03	0.02	1.7	155	57	2.6	0.04	12	3,356

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[1] Plant has divided process wastewaters into two or more outfalls. Pollutants summed in proportion to stream flow.
[2] Represents only portion of total plant discharge of process water.

TABLE V-13

EFFLUENT CHARACTERISTICS AFTER APPLICATION OF END-OF-PIPE TREATMENTS - POLLUTANT AMOUNTS

Plant Code	See Note	Sampled By	Hydraulic Load, liters/1,000 sq m (gal/1,000 sq ft)	Pollutant Amount, kg/1,000 sq m (lb/1,000 sq ft)			
				Cyanide	Cadmium	Chromium	Silver
0045	2	Self	288,000 (7,060)	--	--	--	0.36 (0.073)
1465	1, 3	Self	286,000 (7,030)	11 (2.2)	--	--	0.21 (0.042)
1465	1, 3	EPA	286,000 (7,030)	4.2 (0.86)	<0.015 (0.003)	--	0.054 (0.011)
2714	1, 4	Self	15,500 (380)	0.63 (0.13)	--	--	5×10^{-4} (1×10^{-4})
2714	1, 3	EPA	23,900 (587)	8.3 (1.7)	4.1×10^{-4} (8.3×10^{-5})	--	0.063 (0.013)
7781	2	Self	7,500 (184)	--	0.0015 (3×10^{-4})	--	0.042 (0.0085)
7781	2	EPA	5,010 (123)	--	1.5×10^{-4} (3×10^{-5})	--	0.0088 (0.0018)

1 - Plant uses end-of-pipe treatments on portion of process wastewaters.
2 - Plant uses end-of-pipe treatments on all process wastewaters.
3 - Plant has divided process waste into two or more outfalls. Pollutants summed in proportion to stream flow.
4 - Represents only portion of total plant discharge of process water.

TABLE V-13
(continued)

Plant Code	Pollutant Amount, kg/1,000 sq m (lb/1,000 sq ft)						
	TOC	BOD	Nitrogen-Ammonia	Iron	Lead	TSS	TDS
0045	--	--	--	--	--	--	--
1465	30.7 (6.3)	44.4 (9.09)	2.13 (0.66)[2]	1.46 (0.30)	--	1.86 (0.38)	202.6 (41.5)
1465	17.4 (3.57)	16.1 (3.3)	4.30 (0.88)	1.56 (0.32)	--	0.29 (0.06)	134.8 (27.6)
2714	--	0.1 (0.03)	--	--	--	--	3.4 (0.69)
2714	16.1 (3.29)	26.9 (5.51)	8.35 (1.71)	0.95 (0.195)	0.0015 (3×10^{-4})	1.11 (0.228)	75.2 (15.4)
7781	--	0.83 (0.17)	--	0.13 (0.026)	0.0015 (3×10^{-4})	0.31 (0.063)	--
7781	0.78 (0.16)	0.77 (0.158)	0.28 (0.058)	0.013 (0.0027)	2×10^{-4} (4×10^{-5})	0.059 (0.012)	16.8 (3.44)

SECTION VI

SELECTION OF POLLUTANT PARAMETERS

The Agency is concerned over potential discharges of toxic pollutants from industrial sources. A comprehensive effort was conducted to determine if these pollutants are present in wastewaters from photographic processing. The toxic pollutants are listed in Table VI-1. The conventional parameters listed in Table VI-2 and non-conventional parameters listed in Table VI-3 were also selected to be sought in the field data collection program. In addition, related published data and NPDES permit applications for direct discharges in this industry were examined to assist in this determination.

The wastewater characterization detailed in the previous section has been reviewed to determine what wastewater constituents are contributed to photoprocessing wastewater in significant quantities. A toxic pollutant was considered significant unless one or more of the following was true:

(a) the pollutant was not detected,
(b) its presence was due to incoming water, or
(c) it was present in concentrations below current water quality criteria.

TABLE VI-1
Toxic Pollutants

acenapthene
acrolein
acrylonitrile
benzene
benzidine
carbon tetrachloride (tetrachloromethane)
chlorobenzene
1,2,4-trichlorobenzene
hexachlorobenzene
1,2-dichloroethane
1,1,1-trichloroethane
hexachloroethane
1,1-dichloroethane
1,1,2-trichloroethane
1,1,2,2-tetrachloroethane
chloroethane
bis(chloromethyl)ether
bis(2-chloroethyl) ether
2-chloroethyl vinyl ether (mixed)
2-chloronapthalene
2,4,6-trichlorophenol
parachlorometa cresol
chloroform (trichloromethane)
2-chlorophenol
1,2-dichlorobenzene
1,3-dichlorobenzene
1,4-dichlorobenzene
3,3'-dichlorobenzidine
1,1-dichloroethylene
2,4-dichlorophenol
1,2-dichloropropane
1,2-dichloropropylene (1,3-dichloropropene)
2,4-dimethylphenol
2,4-dinitrotoluene
2,6-dinitrotoluene
1,2-diphenylhydrazine
ethylbenzene
fluoranthene
4-chlorophenyl phenyl ether
4-bromophenyl phenyl ether
bis(2-chloroisopropyl) ether
bis(2-chloroethoxy) methane
methylene chloride (dichloromethane)
methyl chloride (chloromethane)
methyl bromide (bromomethane)
bromoform (tribromomethane)
dichlorobromomethane
trichlorofluoromethane
dichlorodifluoromethane
chlorodibromomethane
hexachlorobutadiene
hexachlorocyclopentadiene
isophorone
napthalene
nitrobenzene
2-nitrophenol
4-nitrophenol
2,4-dinitrophenol
4,6-dinitro-o-cresol
N-nitrosodimethylamine
N-nitrosodiphenylamine
N-nitrosodi-n-propylamine
pentachlorophenol
phenol
bis(2-ethylhexyl) phthalate
butyl benzyl phthalate
di-n-butyl phthalate
di-n-octyl phthalate
diethyl phthalate
dimethyl phthalate
benzo(a)anthracene (1,2-benzanthracene)
benzo(a)pyrene(3,4-benzopyrene)
3,4-benzofluoranthene
benzo(k)fluoranthene (11,12-benzofluoranthene)
chrysene
acenaphthylene

TABLE VI-1 (continued)

anthracene
benzo(ghi)perylene(1,12-benzoperylene)
fluorene
phenanthrene
dibenzo(a,h)anthracene (1,2,5,6-dibenzanthracene)
indeno(1,2,3-cd) pyrene (2,3-o-phenylenepyrene)
pyrene
tetrachloroethylene
toluene
trichloroethylene
vinyl chloride (chloroethylene)
aldrin
dieldrin
chlordane
4,4^1-DDT
4,4^1-DDE(p,p^1-DDX)
4,4^1-DDD(p,p^1-TDE)
a-endosulfan-Alpha
b-endosulfan-Beta
endosulfan sulfate
endrin
endrin aldehyde
heptachlor
heptachlor epoxide
a-BHC-Alpha
b-BHC-Beta
r-BHC-(lindane)Gamma
g-BHC-Delta
PCB-1242 (Arochlor 1242)
PCB-1254 (Arochlor 1254)
PCB-1221 (Arochlor 1221)
PCB-1232 (Arochlor 1232)
PCB 1248 (Arochlor 1248)
PCB-1260 (Arochlor 1260)
PCB-1016 (Arochlor 1016)
toxaphene
antimony (total)
arsenic (total)
asbestos (fibrous)
beryllium (total)
cadmium (total)
chromium (total)
copper (total)
cyanide (total)
lead (total)
mercury (total)
nickel (total)
selenium (total)
silver (total)
thallium (total)
zinc (total)

TABLE VI-2
Conventional Pollutants

pH
BOD
COD
Oil and Grease
Suspended Solids

TABLE VI-3
Non-Conventional Pollutants

Acidity
Alkalinity
Carbon, organic (TOC)
Chlorinated Hydrocarbons
Color (units)
Cyanide (am. chlorin.)
DO
$Fe(CN)_6$
Fluoride
Halides
Hydroquinone
Nitrogen-
  Ammonia
Phenols
Silica
Solids -
  Total
  Dissolved
  Volatile
Specific conductance

Sulfate
Sulfite/Thiosulfate
Surfactants
Thiocyanate
Turbidity (units)
Aluminum
Barium
Boron
Calcium
Chromium^{+6}
Cobalt
Iron
Magnesium
Manganese
Molybdenum
Potassium
Sodium
Tin
Titanium

Wastewaters from plants 6208, 2714, 4550 and 7781 were examined for toxic pollutants. No organic toxic pollutants were found except 1,2-diphenylhydrazine, which was found (200 ug/l) in one stream at plant 2714. This chemical was found in the reverse osmosis permeate but was absent in the reverse osmosis concentrate, raising the possibility that its presence in the permeate was an anomaly. This pollutant was not found at any other plant. The organic priority pollutants were measured to a detectability limit of 20 ug/l by gas chromatograph-mass spectrometer analysis.

Pesticides were found at low levels at four of the five plants. Amounts varied from the detection limit up to 1.6 ug/l. Similar amounts of pesticides were also found in the incoming water supply in these plants. The quantitation limit for pesticides is 0.1 ug/l with the instrumentation used. The single effluent streams from plants 6208, 4550 and 7781 and all three outfalls for plant 2714 were analyzed for asbestos, but none was found.

The following toxic metals were not found above their detectable limits in plant effluents:

Metal	Detectable Limit, mg/l
Arsenic	0.002
Beryllium	0.005
Copper	0.010
Mercury	0.0002
Nickel	0.020
Selenium	0.002
Thallium	0.100

Antimony and zinc were found in concentrations equivalent to concentrations in incoming water supply or equal to, or less than, current water quality criteria.

A discussion of those conventional and toxic pollutant parameters which were found in significant quantity follows. Table VI-4 lists these parameters.

TABLE VI-4
Pollutants Found in Significant Quantities in
Effluents from Photographic Processing Plants

Toxic	Conventional	Non-Conventional
Cadmium	pH	Boron
Chromium	BOD	Dissolved Solids
Cyanide, total	COD	Halides
Lead		Iron
Silver		Nitrogen, ammonia
		Phenols
		Sulfate
		TOC

DESCRIPTION OF POLLUTANT PARAMETERS OF SIGNIFICANCE

I. POLLUTANT PROPERTIES

Acidity and Alkalinity - pH

Although not a specific pollutant, pH is related to the acidity or alkalinity of a wastewater stream. It is not a linear or direct measure of either;, however, it may properly be used as a surrogate to control both excess acidity and excess alkalinity in water. The term pH is used to describe the hydrogen ion - hydroxyl ion balance in water. Technically, pH is the hydrogen ion concentration or activity present in a given solution. pH numbers are the negative logarithm of the hydrogen ion concentration. A pH of 7 generally indicates neutrality or a balance between free hydrogen and free hydroxyl ions. Solutions with a pH above 7 indicate that the solution is alkaline, while a pH below 7 indicates that the solution is acid.

Knowledge of the pH of water or wastewater is useful in determining necessary measures for corrosion control, pollution control, and disinfection. Waters with a pH below 6.0 are corrosive to water works structures, distribution lines, and household plumbing fixtures, and such corrosion can add constituents to drinking water such as iron, copper, zinc, cadmium, and lead. Low pH waters not only tend to dissolve metals from structures and fixtures but also tend to redissolve or leach metals from sludges and bottom sediments. The hydrogen ion concentration can affect the "taste" of the water and at a low pH, water tastes "sour."

Extremes of pH or rapid pH changes can exert stress conditions or kill aquatic life outright. Even moderate changes from "acceptable" criteria limits of pH are deleterious to some species. The relative toxicity* to aquatic life of many materials is increased by changes in the water pH. For example, metalocyanide complexes can increase a thousandfold in toxicity with a drop of 1.5 pH units. Similarly, the toxicity of ammonia is a function of pH. The bactericidal effect of chlorine in most cases is less as the pH increases, and it is economically advantageous to keep the pH close to 7.

Photographic processing wastewaters from the individual processing steps are both basic and acidic. For example, developers are basic and the stop and fix solutions are acidic. When waste streams from these solutions are combined in the plant discharge, the different streams tend to neutralize each other. Overall plant discharges in this industry are generally in the pH range of 6 to 9 with most in the range of 7 to 8.5.

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* The term toxic or toxicity is used herein in the normal scientific sense of the word and not as a specialized term referring to Section 307(a) of the Act.

Acidity is defined as the quantitative ability of a water to neutralize hydroxyl ions. It is usually expressed as the calcium carbonate equivalent of the hydroxyl ions neutralized. Acidity should not be confused with pH value. Acidity is the quantity of hydrogen ions which may be released to react with or neutralize hydroxyl ions while pH is a measure of the free hydrogen ions in a solution at the instant the pH measurement is made. A property of many chemicals, called buffering, may hold hydrogen ions in a solution from being in the free state and being measured as pH. The bond of most buffers is rather weak, and hydrogen ions tend to be released from the buffer as needed to maintain a fixed pH value.

Highly acid waters are corrosive to metals, concrete, and living organisms, exhibiting the pollutional characteristics outlined above for low pH waters. Depending on buffering capacity, water may have a higher total acidity at pH values of 6.0 than other waters with a pH value of 4.0.

Alkalinity is defined as the ability of a water to neutralize hydrogen ions. It is usually expressed as the calcium carbonate equivalent of the hydrogen ions neutralized.

Alkalinity is commonly caused by the presence of carbonates, bicarbonates, hydroxides, and to a lesser extent, by borates, silicates, phosphates, and organic substances. Because of the nature of the chemicals causing alkalinity, and the buffering capacity of carbon dioxide in water, very high pH values are seldom found in natural waters.

Excess alkalinity as exhibited in a high pH value may make water corrosive to certain metals, detrimental to most natural organic materials, and toxic to living organisms.

Ammonia is more lethal with a higher pH. The lacrimal fluid of the human eye has a pH of approximately 7.0, and a deviation of 0.1 pH unit from the norm may result in eye irritation for the swimmer. Appreciable irritation will cause severe pain.

Total Suspended Solids

Suspended solids include both organic and inorganic materials. The inorganic compounds include sand, silt and clay. The organic fraction includes such materials as grease, oil, tar, and animal and vegetable waste products. These solids may settle out rapidly, and bottom deposits are often a mixture of both organic and inorganic solids. Solids may be suspended in water for a time, and then settle to the bed of the stream or lake. These solids discharged with man's wastes may be inert, slowly biodegradable materials, or rapidly decomposable substances. While in suspension, they increase the turbidity of the water, reduce light penetration, and impair the photosynthetic activity of aquatic plants.

Suspended solids in water interfere with many industrial processes, cause foaming in boilers and incrustations on equipment exposed to such water, especially as the temperature rises. They are undesirable in process water used in the manufacture of steel, in the textile industry, in laundries, in dyeing, and in cooling systems. Solids in suspension are aesthetically displeasing. When they settle to form sludge deposits on the stream or lake bed, they are often damaging to the life in water. Solids, when transformed to sludge deposits, may do a variety of damaging things, including blanketing the stream or lake bed and thereby destroying the living spaces for those benthic organisms that would otherwise occupy the habitat. When of an organic nature, solids use a portion or all of the dissolved oxygen available in the area. Organic materials also serve as a food source for sludgeworms and associated organisms.

Disregarding any toxic effect attributable to substances leached out by water, suspended solids may kill fish and shellfish by causing abrasive injuries and by clogging the gills and respiratory passages of various aquatic fauna. Indirectly, suspended solids are inimical to aquatic life because they screen out light, and they promote and maintain the development of noxious conditions through oxygen depletion. This results in the killing of fish and fish food organisms. Suspended solids also reduce the recreational value of the water.

Suspended solids are not normally a problem in this industry. However, suspended solids are generated during some recovery operations such as precipitation of silver sulfide and ferro/ferricyanides. These solids are sometimes recovered for recovery of silver or reuse, respectively.

II. POLLUTANT MATERIALS

Ammonia (NH_3)

Ammonium compounds are used in the photoprocessing industry as constituents in some fix, bleach-fix, and stabilizer solutions. The ammonium ion can be present in these solutions at concentrations of 10 to 100 grams per liter and be present in the plant effluent in concentrations up to 150 mg/l.

Ammonia occurs in surface and ground waters as a result of the decomposition of nitrogenous organic matter. It is one of the constituents of the complex nitrogen cycle. It may also result from the discharge of industrial wastes. Because ammonia may be indicative of pollution and because it increases the chlorine demand, it is recommended that ammonia nitrogen in public water supply sources not exceed 0.5 mg/l.

Ammonia exists in its non-ionized form only at higher pH levels and is most toxic in this state. The lower the pH, the more ionized ammonia is formed, and its toxicity decreases. Ammonia, in the presence of dissolved oxygen, is converted to nitrate (NO_3) by nitrifying bacteria. Nitrite (NO_2), which is an intermediate product between ammonia and nitrate, sometimes occurs in quantity when depressed oxygen conditions permit. Ammonia can exist in several other chemical combinations including ammonium chloride and other ammonia salts.

Nitrates are considered to be among the objectionable components of mineralized waters. Excess nitrates cause irritation to the gastrointestinal tract, causing diarrhea and diuresis. Methemoglobinemia, a condition characterized by cyanosis which can result in infant and animal deaths, can be caused by high nitrate concentrations in waters used for feeding. Evidence exists that ammonia exerts a toxic effect on all aquatic life depending upon the pH, dissolved oxygen level, and the total ammonia concentration in the water. A significant oxygen demand can result from the microbial oxidation of ammonia. Approximtely 4.5 grams of oxygen are required for every gram of ammonia that is oxidized. Ammonia can add to eutrophication problems by supplying nitrogen to aquatic life. Ammonia can be toxic, exerts an oxygen demand, and contributes to eutrophication.

Boron (B) Boron compounds, in the form of borates, are used in developers, bleaches, and fixers in concentrations up to one hundred grams per liter. After mixing of the various waste solutions, the amount of boron in the plant effluent generally ranges from 1 to 10 mg/l.

Never found in nature in its elemental form, boron occurs as sodium borate (borax) or as calcium borate (colemanite) in mineral deposits and natural waters of Southern California and Italy. Elemental boron is used in nuclear installations as a shielding material (neutron absorber). It is also used in metallurgy to harden other metals.

Boric acid and boron salts are used extensively in industry for such purposes as weatherproofing wood, fireproofing fabrics, manufacturing glass and porcelain, and producing leather, carpets, cosmetics, and artificial gems. Boric acid is used as a bactericide and fungicide and boron, in the form of boron hydrides or borates, is used in high energy fuels.

Boron is present in the ordinary human diet at about 10 to 20 mg/day, with fruits and vegetables being the largest contributors. In food or in water, it is rapidly and completely absorbed by the human system, but it is also promptly excreted in urine. Boron in drinking water is not generally regarded as a hazard to humans. It has been reported that boron concentrations up to 30 mg/l are not harmful.

Bromide (Br)

Bromides are derived from hydrobromic acid (HBr). Bromide properties are similar to those of chlorides and iodides. Bromides are usually produced from bromine, which in turn is obtained from salt brines or sea water.

Bromides are used in medicine as sedatives in the treatment of nervous disorders. Silver bromide is used in photographic films and paper, and bromide compounds are present in the formulations of bleaches.

Cadmium (Cd)

Cadmium occurs in some, but not all photoprocessing facilities, because it is an ingredient in some sensitized products. The cadmium compounds are at least partially removed during the development portion of the process and are primarily found in the waste developer.

Cadmium is a relatively rare element that is seldom found in sufficient quantities in a pure state to warrant mining or extraction from the earth's surface. It is found in trace amounts of about 1 ppm throughout the earth's crust. Cadmium is, however, a valuable by-product of zinc production.

Cadmium is used primarily as a metal plating material and can be found as an impurity in the secondary refining of zinc, lead, and copper. Cadmium is also used in the manufacture of primary and storage batteries and as a neutron adsorber in nuclear reactors. Other uses of cadmium are in the production of pigments, phosphors, semi-conductors, electrical conductors, and special purpose low temperature alloys.

Cadmium is an extremely dangerous cumulative toxicant, causing insidious progressive chronic poisoning in mammals, fish, and probably other animals because the metal is not excreted. Cadmium could form organic compounds which might lead to mutagenic or teratogenic effects. Cadmium is known to have marked acute and chronic effects on aquatic organisms also.

Toxic effects of cadmium on man have been reported from throughout the world. Cadmium is normally ingested by humans through food and water and also by breathing air contaminated by cadmium. Cadmium in drinking water supplies is extremely hazardous to humans, and conventional treatment, as practiced in the United States, does not remove it. Cadmium is cumulative in the liver, kidney, pancreas, and thyroid of humans and other animals. A severe bone and kidney syndrome in Japan has been associated with the ingestion of as little as 600 µg/day of cadmium. The allowable cadmium concentration in drinking water is set as low as 0.01 mg/l in the U.S. and as high as 0.10 mg/l in Russia.

Cadmium acts synergistically with other metals. Copper and zinc substantially increase its toxicity. Cadmium is concentrated by marine organisms, particularly mollusks which accumulate cadmium in calcareous tissues and in the viscera. A concentration factor of 1,000 for cadmium in fish muscle has been reported, as have concentration factors of 3,000 in marine plants, and up to 29,600 in certain marine animals. The eggs and larvae of fish are apparently more sensitive than adult fish to poisoning by cadmium, and crustaceans appear to be more sensitive than fish eggs and larvae.

Chlorides

Chlorides are found in practically all natural waters. They may be: (a) of natural mineral origin or derived from a sea-water contamination of underground supplies, (b) salts spread on fields for agricultural purposes, (c) human or animal sewage, or (d) industrial effluents, such as those from paper works, galvanizing plants, water softening plants, oil wells, and petroleum refineries.

The human tolerance for chlorides varies with climate and exertion. Chlorides lost through perspiration are replaced by chlorides in either the diet or drinking water. From hot dry areas, there are reports that chloride concentrations up to almost 900 mg/l have not been harmful. Chloride concentrations of 1,500 mg/l are reported to be safe for cattle, sheep, swine and chickens. Also, 2,000 mg/l of chloride has been reported as not harmful to some fish.

Because of their non-toxic nature, chlorides are not selected as a pollutant parameter requiring the establishment of a limitation.

Chromium (Cr)

Sodium and potassium dichromate are principal constituents of certain bleaches used primarily in the color movie print film process. These compounds in combination with bromide ions oxidize the developed silver to silver bromide. A dichromate bleach may also be used in the black and white reversal process. Again, the primary application for this process is in the movie industry.

Chromium is an elemental metal usually found as a chromite ($FeCr_2O_4$). The metal is normally processed by reducing the oxide with aluminum. Chromium and its compounds are used extensively throughout industry. It is used to harden steel and as an ingredient in other useful alloys. Chromium is also used in the electroplating industry as an ornamental and corrosion resistant plating on steel and can be used in pigments and as a pickling acid (chromic acid). It is used in certain chromate bleaches in the photographic processing industry.

The two most prevalent chromium forms found in industry wastewaters are hexavalent and trivalent chromium. Dichromate compounds used in the photographic processing industry are hexavalent chromium compounds which are partially reduced to the trivalent form during use. Chromium can exist as either trivalent or hexavalent compounds in raw waste streams, although most of the hexavalent chromium is reduced to the trivalent form when mixed with other photographic processing wastes, particularly sulfites and thiosulfates. Hexavalent chromium treatment involves reduction to the trivalent form prior to removal of chromium from the waste stream as a hydroxide precipitate.

Chromium, in its various valence states, is hazardous to man. It can produce lung tumors when inhaled and induces skin sensitizations. Large doses of chromates have corrosive effects on the intestinal tract and can cause inflammation of the kidneys. Levels of chromate ions that have no effect on man appear to be so low as to prohibit determination to date. The recommendation for public water supplies is that such supplies contain no more than 0.05 mg/l total chromium.

THe toxicity of chromium salts to fish and other aquatic life varies widely with the species, temperature, pH, valence of the chromium and synergistic or antagonistic effects, especially those of hard water. Studies have shown that trivalent chromium is more toxic to fish of some types than hexavalent chromium. Other studies have shown opposite effects. Fish food organisms and other lower forms of aquatic life are extremely sensitive to chromium, and it also inhibits the growth of algae. Therefore, both hexavalent and trivalent chromium must be considered harmful to particular fish or organisms.

Chromium is not destroyed when treated by a POTW (although the oxidation state may change), and either passes through to the POTW effluent or is incorporated into the POTW sludge. Both oxidation states can cause POTW treatment inhibition and can also limit the usefulness of municipal sludge. Hexavalent and trivalent chromium both cause toxic effects in a wide variety of organisms including aquatic species and humans. Chromium which passes through a POTW becomes a potential drinking and bathing water contaminant. Hexavalent chromium is a known human carcinogen, and is generally the more toxic of the two oxidation states. As a result of these considerations, chromium pretreatment standards must be the same as discharge limitations for direct discharge.

Cyanide (CN)

Cyanide is a compound that is widely used in industry primarily as sodium cyanide (NaCN) or hydrocyanic acid (HCN). The major use of cyanides is in the electroplating industry where cyanide baths are used to hold ions such as zinc and cadmium in solution. Cyanides in various compounds are also used in steel plants, chemical plants, textile dyeing, and ore processing.

Cyanides in the form of an iron-cyanide complex are used in the photographic processing industry. This complex, usually sodium or potassium ferricyanide, is a major constituent of a commonly used color bleach which oxidizes the metallic silver image to a silver halide. During the process a portion of the ferricyanide ions is reduced to ferrocyanide, and the waste bleach contains a mixture of ferri-ferrocyanide (hexacyanoferrate) ions.

The hexacyanoferrate ions exhibit a low order of toxicity to aquatic species. Acute static bioassay tests performed by exposing fathead minnows (Pimephales promelas) to various concentrations of the ferrocyanide ion resulted in a 96-hour LC_{50} value of greater than 100 ppm. (The 96-hour LC_{50} value is the chemical concentration that will cause a 50 percent mortality of the test species after the 96-hour exposure.) Similar tests with lower forms of aquatic life did show greater sensitivity, i.e., 96-hour LC_{50} values of 0.1 to 1 ppm for crustaceans (Daphnia magna) and algae growth was inhibited at ferrocyanide concentrations of 1 to 10 ppm. It has been shown that the hexacyanoferrate ions are photochemically active and readily release the cyanide ion with sunlight exposure. Bioassay tests with 8,000 foot candles of simulated sunlight resulted in 50 percent minnow fatalities in about five hours at a 100 ppm ferrocyanide concentration. This photochemical effect is of concern for those facilities which use ferricyanide bleach and discharge the wastewater directly to surface waters.

The large majority of photoprocessing facilities discharge to POTW's. Laboratory and on-site treatment plant tests have shown that the hexacyanoferrate ions cause no adverse effects on the biomass and are resistant to biological degradation. The treatment plant removal efficiency was reported to be greater than 60 percent. The hexacyanoferrate ions are probably precipitated in the presence of iron, zinc, or calcium ions and are combined with the waste sludge.

Land disposal is a common disposal method for POTW sludges. The fate of the hexacyanoferrates under land disposal conditions has been evaluated with leachate tests in the laboratory. Such tests were performed using several soil types and several test sludges ranging in total cyanide content from 9 to 37,000 mg/kg (dry basis). Evaluation of the elutriate showed no release, and column tests showed that the hexacyanoferrates were released from the sludge in particulate form and were bound within the soil by adsorption and filtration.

Of all the cyanides, hydrogen cyanide (HCN) is probably the most acutely lethal compound. HCN dissociates in water to hydrogen ions and cyanide ions in a pH dependent reaction. The cyanide ion is less acutely lethal than HCN. The relationship of pH to HCN shows that as the pH is lowered to below 7, there is less than 1 percent of the cyanide molecules in the form of the CN ion and the rest is present as HCN. When the pH is increased to 8, 9, and 10, the percentage of cyanide present as CN ion is 6.7, 42 and 87 percent, respectively. The toxicity of cyanides is also increased by increases in temperature and reductions in oxygen tensions. A temperature rise of 10°C produced a two to threefold increase in the rate of the lethal action of cyanide.

In the body, the CN ion, except for a small portion exhaled, is rapidly changed into a relatively non-toxic complex (thiocyanate) in the liver and eliminated in the urine. There is no evidence that the CN ion is stored in the body. The safe ingested limit of cyanide has been estimated at something less than 18 mg/day, part of which comes from normal environment and industrial exposure. The average fatal dose of HCN by ingestion by man is 50 to 60 mg. It has been recommended that a limit of 0.2 mg/l cyanide not be exceeded in public water supply sources.

The harmful effects of the cyanides on aquatic life are affected by the pH, temperature, dissolved oxygen content, and the concentration of minerals in the water. The biochemical degradation of cyanide is not affected by temperature in the range of 10°C to 35°C while the toxicity of HCN is increased at higher temperatures.

On lower forms of life and organisms, cyanide does not seem to be as toxic as it is toward fish. The organisms that digest BOD were found to be inhibited at 1.0 mg/l and at 60 mg/l although the effect is more one of delay in exertion of BOD than total reduction.

Dissolved Solids

In natural waters, the dissolved solids are mainly carbonates, chlorides, sulfates, phosphates, and to a lesser extent, nitrates of calcium, magnesium, sodium, and potassium, with traces of iron, manganese, and other substances. The summation of all individual dissolved solids is commonly referred to as total dissolved solids.

Many communities in the United States and in other countries use water supplies containing 2,000 to 4,000 mg/l of dissolved salts, when no better water is available. Such waters are not palatable, may not quench thirst, and may have a laxative action on new users. Waters containing more than 4,000 mg/l of total salts are generally considered unfit for human use, although in hot climates such higher salt concentrations can be tolerated. Waters containing 5,000 mg/l or more are reported to be bitter and act as a bladder and intestinal irritant. It is generally agreed that the salt concentration of good, palatable water should not exceed 500 mg/l.

Limiting concentrations of dissolved solids for fresh-water fish may range from 5,000 to 10,000 mg/l, depending on species and prior acclimatization. Some fish are adapted to living in more saline waters, and a few species of fresh-water forms have been found in natural waters with a salt concentration of 15,000 to 20,000 mg/l. Fish can slowly become acclimatized to higher salinities, but fish in waters of low salinity cannot survive sudden exposure to high salinities, such as those resulting from discharges of oil well brines. Dissolved solids may influence the toxicity of heavy metals and organic compounds to fish and other aquatic life, primarily because of the antagonistic effect of hardness on metals.

Waters with total dissolved solids (TDS) concentrations higher than 500 mg/l have decreasing utility as irrigation water. At 5,000 mg/l, water has little or no value for irrigation.

Dissolved solids in industrial water uses can cause foaming in boilers and can cause interferences with cleanliness, color, or taste of many finished products. High concentrations of dissolved solids also tend to accelerate corrosion. Most of the solids present in photoprocessing wastewater are dissolved.

Specific conductance is a measure of the capacity of water to convey an electric current. This property is related to the total concentration of ionized substances in water and to the water temperature. This property is frequently used as a substitute method of quickly estimating the dissolved solids concentration.

Iron (Fe)

Iron is an abundant metal found in the earth's crust. The most common iron ore is hematite from which iron is obtained by reduction with carbon. Other forms of commercial ores are magnetite and taconite. Pure iron is not often found in commercial use, but it is usually alloyed with other metals and minerals, the most common being carbon.

Iron is the basic element in the production of steel and steel alloys. Iron with carbon is used for casting of major parts of machines, and it can be machined, cast, formed, and welded. Ferrous iron is used in paints, while powdered iron can be sintered and used in powder metallurgy. Iron compounds are also used to precipitate other metals and undesirable minerals from industrial wastewater streams. The dissolved iron present in photoprocessing wastewaters comes from two sources. Iron compounds are used as bleaches, and iron is added to wastewater by metallic replacement silver recovery processes.

Iron is chemically reactive and corrodes rapidly in the presence of moist air and at elevated temperatures. In water and in the presence of oxygen, the resulting products of iron corrosion may be pollutants in water. Natural pollution occurs from the leaching of soluble iron salts from soil and rocks and is increased by industrial wastewater from pickling baths and other solutions containing iron salts.

Corrosion products of iron in water cause staining of porcelain fixtures, and ferric iron combines with the tannin to produce a dark violet color. The presence of excessive iron in water discourages cows from drinking and, thus, reduces milk production. High concentrations of ferric and ferrous ions in water kill most fish introduced to the solution within a few hours. The killing action is attributed to coatings of iron hydroxide precipitates on the gills. Iron oxidizing bacteria are dependent on iron in water for growth. These bacteria form slimes that can affect the aesthetic values of bodies of water and cause stoppage of flows in pipes.

Iron is an essential nutrient and micronutrient for all forms of growth. Drinking water standards in the U.S. have set a recommended limit of 0.3 mg/l of iron in domestic water supplies based not on the physiological considerations, but rather on aesthetic and taste considerations of iron in water.

Lead (Pb)

Lead is used in various solid forms both as a pure metal and in several compounds. Lead appears in some natural waters, especially in those areas where mountain limestone and galena are found. Lead can also be introduced into water from lead pipes by the action of the water on the lead. Lead is not knowingly added to process wastewater in this industry.

Lead is a toxic material that is foreign to humans and animals. The most common form of lead poisoning is called plumbism. Lead can be introduced into the body from the atmosphere containing lead or from food and water. Lead cannot be easily excreted and is cumulative in the body over long periods of time, eventually causing lead poisoning with the ingestion of an excess of 0.6 mg per day over a period of years. It has been recommended that 0.05 mg/l lead not be exceeded in public water supply sources.

Chronic lead poisoning has occurred among animals at levels of 0.18 mg/l of lead in soft water and by concentrations under 2.4 mg/l in hard water. Farm animals are poisoned by lead more frequently than any other poison. Sources of this occurrence include paint and water with the lead in solution as well as in suspension. Each year thousands of wild water fowl are poisoned from lead shot that is discharged over feeding areas and ingested by the water fowl. The bacterial decomposition of organic matter is inhibited by lead at levels of 0.1 to 0.5 mg/l.

Fish and other marine life have had adverse effects from lead and salts in their environment. Experiments have shown that small concentrations of heavy metals, especially of lead, have caused a film of coagulated mucus to form first over the gills and then over the entire body probably causing suffocation of the fish. Toxicity of lead is increased with a reduction of dissolved oxygen concentration in the water.

Phenols

Phenols, defined as hydroxy derivatives of benzene and its condensed nuclei, may occur in domestic and industrial wastewater and in drinking water supplies. Chlorination of such waters can produce odoriferous and objectionable tasting chlorophenols.

Although described in the technical literature simply as phenols, the phenol waste category can include a wide range of similar chemical compounds. In terms of pollution control, reported concentrations of phenols are the result of a standard methodology which measures a general group of similar compounds rather than being based upon specific identification of the single compound, phenol (hydroxybenzene). Some of the compounds used in photoprocessing which might be identified as phenols will not respond to standard analytical tests for phenols and do not impart taste to water after chlorination.

Phenols are used in some cutting oils and in the molding of plastics. Cutting fluids can contain phenolic compounds since these materials are normal constituents of hydrocarbon mixtures. In addition, phenolic compounds are added to oils as preservatives or for odor control. They also are found in the wastewaters from the petroleum industry and from certain products of the organic chemical industry.

Phenolic compounds may adversely affect fish in two ways: first, by a direct toxic action, and second, by imparting a taste to the fish flesh. The toxicity of phenol towards fish increases as the dissolved oxygen level is diminished, as the temperature is raised, and as the hardness is lessened. Phenol appears to act as a nerve poison causing too much blood to get to the gills and to the heart cavity and is reported to have a toxic threshold of 0.1-15 mg/l.

Mixed phenolic substances appear to be especially troublesome in imparting taste to fish flesh. Chlorophenol produces a bad taste in fish far below lethal or toxic doses. Threshold concentrations for taste or odor in chlorinated water supplies have been reported as low as 0.00001-0.001 mg/l. Phenols in concentrations of only one part per billion have been known to affect water supplies.

The ingestion of concentrated solutions of phenol by humans results in severe pain, renal irritation, shock, and possibly death. A total dose of 1.5 grams may be fatal. Phenols can be metabolized and oxidized in waste treatment facilities containing organisms acclimated to the phenol concentration in the wastes.

Silver (Ag)

The emulsion on photographic film and paper contains as a principal ingredient various silver halides which form or assist in the formation of the photographic image. During processing a portion (black and white materials) or all (color materials) of the silver is removed from the emulsion by the fix solution. A principal constituent of the fix solution is the thiosulfate ion which forms a complex with silver. The silver thiosulfate complex is stable (it has a dissociation constant of 3.5×10^{-14}) and non-toxic to fish (bioassay test showed no effect on fathead minnows after 96 hours of exposure to the silver thiosulfate complex at concentrations up to 50 mg/l as silver).

Since the large majority of the photoprocessing industry discharges to POTW's, the major concern is the fate of the complex after secondary treatment. Studies have shown that the secondary treatment microorganisms convert the complex to silver sulfide and some metallic silver, most of which is removed from the wastewater stream by settling. The portion that remains with the wastewater exists as colloidal suspensions of silver sulfide and silver and a small fraction of soluble ionic silver. Silver sulfide is insoluble under normal environmental conditions. Bioassay tests have shown it to be non-toxic to fathead minnows. Dynamic 96-hour LC_{50} tests for silver sulfide showed no fatalities at a maximum total silver concentration of 250 ppm.

The silver sulfide and silver that settles is removed from the treatment plant as a constituent of the sludge. Land disposal by landspreading or landfilling is a common disposal method for POTW sludges. Laboratory leachate testing on test sludges containing silver in concentrations from 19 to 83,000 mg/kg (dry) showed no release of silver to the elutriate. Column tests indicated that the silver was effectively bound by the various soil types.

Silver is a soft, lustrous white metal that is insoluble in water and alkali. It is readily ionized by electrolysis and has a particular affinity for sulfur and halogen elements. In nature, silver is found in the elemental state and combined in ores such as argentite (Ag_2S), horn silver ($AgCl$), proustite (Ag_3AsS_3), and pyrargyrite (Ag_3SbS_3).

From these ores, silver ions may be leached into ground waters and surface waters, but since many silver salts such as the chloride, sulfide, phosphate, and arsenate are insoluble, silver ions do not usually occur in significant concentration in natural waters.

Silver is used extensively in electroplating, photographic supplies manufacture, electrical equipment manufacture, soldering and brazing, and battery manufacture. Of these, the two major sources of silver wastes are the photographic and electroplating industries with about 30 percent of U.S. industrial consumption of silver going into the photographic industry. Silver is also used in its basic metal state for such items as jewelry and electrical contacts.

Silver compounds can be absorbed in the circulatory system and reduced silver deposited in the various tissues of the body. A condition known as argyria, a permanent greyish pigmentation of the skin and mucous membranes, can result. Concentrations in the range of 0.4-1 mg/l have caused pathologic changes in the kidneys, liver and spleen of rats.

Silver is recognized as a bactericide, and doses as low as 0.000001 to 0.5 mg/l have been reported as sufficient to sterilize water.

Sulfates

Sulfates occur naturally in waters, particularly in the western United States, as a result of leachings from gypsum and other common materials. They also occur as the final oxidized state of sulfides, sulfites, and thiosulfates. Sulfates may also be present as the oxidized state of organic matter in the sulfur cycle, but they in turn may serve as sources of energy for sulfate splitting bacteria. Sulfates may also be discharged in numerous industrial wastes, such as those from tanneries, sulfate-pulp mills, textile mills, and other plants that use sulfates or sulfuric acid. Thiosulfates occur in photoprocessing wastewater as part of the fix.

In moderate concentrations, sulfates are not harmful, and it has been reported that concentrations up to 1,000 mg/l are harmless. Irrigation concentrations less than 336 mg/l are considered to be good to excellent.

Because of their relatively harmless nature, sulfates are not selected as a pollutant parameter requiring the establishment of a limitation.

Oxygen Demand (BOD, COD, and TOC)

Oxygen Demand

Organic and some inorganic compounds can cause an oxygen demand to be exerted in a receiving body of water. Indigenous microorganisms utilize the organic wastes as an energy source and oxidize the organic matter. In doing so their natural respiratory activity will utilize the dissolved oxygen.

Dissolved oxygen (DO) in water is a quality that, in appropriate concentrations, is essential not only to keep organisms living but also to sustain species reproduction, vigor, and the development of populations. Organisms undergo stress at reduced DO concentrations that makes them less competitive and less able to sustain their species within the aquatic environment. For example, reduced DO concentrations have been shown to interfere with fish population through delayed hatching of eggs, reduced size and vigor of embryos, production of deformities in young, interference with food digestion, acceleration of blood clotting, decreased tolerance to certain toxicants, reduced food utilization efficiency, growth rate, and maximum sustained swimming speed. Other organisms are likewise affected adversely during conditions of decreased DO. Since all aerobic aquatic organisms need a certain amount of oxygen, the consequences of total depletion of dissolved oxygen due to a high oxygen demand can kill all the inhabitants of the affected aquatic area.

It has been shown that fish may, under some natural conditions, become acclimatized to low oxygen concentrations. Within certain limits, fish can adjust their rate of respiration to compensate for changes in the concentration of dissolved oxygen. It is generally agreed, moreover, that those species which are sluggish in movement (e.g., carp, pike, eel) can withstand lower oxygen concentrations than fish which are more lively in habit (such as trout or salmon).

The lethal effect of low concentrations of dissolved oxygen in water appears to be increased by the presence of toxic substances, such as ammonia, cyanides, zinc, lead, copper, or cresols. With so many factors influencing the effect of oxygen deficiency, it is difficult to estimate the minimum safe concentrations at which fish will be unharmed under natural conditions. Many investigations seem to indicate that a DO level of 5.0 mg/l is desirable for a good aquatic environment and higher DO levels are required for selected types of aquatic environments.

Biochemical oxygen demand is the quantity of oxygen required for the biological and chemical oxidation of waterborne substances under ambient or test conditions. Materials which may contribute to the BOD include: carbonaceous organic materials usable as a food source by aerobic organisms; oxidizable nitrogen derived from nitrites, ammonia, and organic nitrogen compounds which serve as food for specific bacteria; and certain chemically oxidizable materials such as ferrous iron, sulfides, and sulfite which will react with dissolved oxygen or which are metabolized by bacteria. In most industrial and municipal wastewaters, the BOD derives principally from organic materials and from ammonia (which is itself derived from animal or vegetable matter).

The BOD of a waste exerts an adverse effect upon the dissolved oxygen resources of a body of water by reducing the oxygen available to fish, plant life, and other aquatic species. Conditions can be reached where all of the dissolved oxygen in the water is utilized resulting in anaerobic conditions and the production of undesirable gases such as hydrogen sulfide and methane. The reduction of dissolved oxygen can be detrimental to fish populations, fish growth rate, and organisms used as fish food. A total lack of oxygen due to the exertion of an excessive BOD can result in the death of all aerobic aquatic inhabitants in the affected area.

Water with a high BOD indicates the presence of decomposing organic matter and associated increased bacterial concentrations that degrade its quality and potential uses. A by-product of high BOD concentrations can be increased algal concentrations and blooms which result from decomposition of the organic matter and which form the basis of algal populations.

The BOD_5 (5-day BOD) test is used widely to estimate the pollutional strength of domestic and industrial wastes in terms of the oxygen that they will require if discharged into receiving streams. The test is an important one in water pollution control activities. It is used for pollution control regulatory activities, to evaluate the designs and efficiencies of wastewater treatment works, and to indicate the state of purification or pollution of receiving bodies of water.

Complete biochemical oxidation of a given waste may require a period of incubation too long for practical analytical test purposes. For this reason, the 5-day period has been accepted as standard, and the test results have been designated as BOD_5. Specific chemical test methods are not readily available for measuring the quantity of many degradable substances and their reaction products. Reliance in such cases is placed on the collective parameter, BOD_5, which measures the weight of dissolved oxygen utilized by microorganisms as they oxidize or transform the gross mixture of chemical compounds in the wastewater. The biochemical reactions involved in the oxidation of carbon compounds are related to the period of incubation. The five-day BOD normally measures only 60 to 80 percent of the carbonaceous biochemical oxygen demand of the sample, and for many purposes this is a reasonable parameter. Additionally, it can be used to estimate the gross quantity of oxidizable organic matter.

The BOD_5 test is essentially a bioassay procedure which provides an estimate of the oxygen consumed by microorganisms utilizing the degradable matter present in a waste under conditions that are representative of those that are likely to occur in nature. Standard conditions of time, temperature, suggested microbial seed, and dilution water for the wastes have been defined and are incorporated in the standard analytical procedure. Through the use of this procedure, the oxygen demand of diverse wastes can be compared and evaluated for pollution potential and to some extent for treatability by biological treatment processes.

Because the BOD test is a bioassay procedure, it is important that the environmental conditions of the test be suitable for the microorganisms to function in an uninhibited manner at all times. This means that toxic substances must be absent and that the necessary nutrients, such as nitrogen, phosphorus, and trace elements, must be present.

Chemical Oxygen Demand (COD)

Chemical oxygen demand is a purely chemical oxidation test devised as an alternate method of estimating the total oxygen demand of a wastewater. Since the method relies on the oxidation-reduction system of chemical analyses rather than on biological factors, it is more precise, accurate, and rapid than the BOD test. The COD test is widely used to estimate the total oxygen demand (ultimate rather than 5-day BOD) to oxidize the compounds in a wastewater. It is based on the fact that organic compounds, with a few exceptions, can be oxidized by strong chemical oxidizing agents under acid conditions with the assistance of certain inorganic catalysts.

The COD test measures the oxygen demand of compounds that are biologically degradable and of many that are not. Pollutants which are measured by the BOD_5 test will be measured by the COD test. In addition, pollutants which are more resistant to biological oxidation will also be measured as COD. COD is a more inclusive measure of oxygen demand than is BOD_5 and will result in higher oxygen demand values than will the BOD_5 test.

The compounds which are more resistant to biological oxidation are becoming of greater and greater concern not only because of their slow but continuing oxygen demand on the resources of the receiving water, but also because of their potential health effects on aquatic life and humans. Many of these compounds result from industrial discharges and some have been found to have carcinogenic, mutagenic and similar adverse effects, either singly or in combination. Concern about these compounds has increased as a result of demonstrations that their long life in receiving water - the result of a slow biochemical oxidation rate - allows them to contaminate downstream water intakes. The commonly used systems of water purification are not effective in removing these types of materials, and disinfection such as chlorination may convert them into even more hazardous materials.

Thus the COD test measures organic matter which exerts an oxygen demand and which may affect the health of the public. It is a useful analytical tool for pollution control activities. It provides a more rapid measurement of the oxygen demand and an estimate of organic compounds which are not measured in the BOD_5 test.

Total organic carbon (TOC) is measured by the catalytic conversion of organic carbon in a wastewater to carbon dioxide. Most organic chemicals have been found to be measured quantitatively by the equipment now in use. The time of analyses is short, from 5 to 10 minutes, permitting a rapid and accurate estimate of the organic carbon content of the wastewaters to be made by relatively unskilled personnel.

A TOC value does not indicate the rate at which the carbon compounds are oxidized in the natural environment. The TOC test will measure compounds that are readily biodegradable and measured by the BOD_5 test as well as those that are not. TOC analyses will include those biologically resistant organic compounds that are of concern in the environment. BOD and COD methods of analyses are based on oxygen utilization of the wastewater. The TOC analyses estimate the total carbon content of a wastewater. There is as yet no fundamental correlation of TOC to either BOD or COD. However, where organic laden wastewaters are fairly uniform, there will be a fairly constant correlation among TOC, BOD and COD. Once such a correlation is established, TOC can be used as an inexpensive test for routine process monitoring.

SECTION VII

CONTROL AND TREATMENT TECHNOLOGIES

Thus far, the Photoprocessing Industry has been characterized with regard to processes used, water use, wastes generated, pollutants of concern, in-process control technologies used, end-of-pipe treatment technologies employed, effluent quality, and wastewater discharge destinations. This section discusses the extent to which the current use of in-process controls and end-of-pipe treatments by this industry reduces pollutant discharge. Other technologies that are either being considered or are possibly applicable for the treatment of wastewater generated by photoprocessors are also discussed.

IN-PROCESS CONTROL TECHNOLOGIES

The control technologies employed by the photoprocessing industry are described in detail in Section III of this document. These consist of process modifications to reduce discharge of expensive materials such as silver and complex cyanide salts. Although these practices are used primarily for resource recovery, their use results in a secondary benefit of reducing the pollutant load in process wastewater.

Recovery and Regeneration Processes

An estimate of the extent of use of some in-process controls and treatments currently used in the industry is shown in Table VII-1.

As shown in Table VII-1, most of the facilities in the four largest size categories recover silver and regenerate ferricyanide bleach. It is also estimated that a similar proportion of the facilities regenerate their ferric EDTA bleach and bleach-fix. Recovery of silver from wash water using ion exchange or reverse osmosis is practiced by only a relatively small number of the larger facilities. An even smaller number of facilities regenerate other solutions such as developers and prewashes. Most facilities which process

TABLE VII-1

ESTIMATED BREAKDOWN OF IN-PROCESS CONTROL AND TREATMENT USE BY PLANT SIZE (DAILY PRODUCTION)

Production sq m/day (sq ft/day)	Production Size Category	Number of Plants	PERCENTAGE OF PLANTS USING INDICATED CONTROLS BY SIZE CATEGORY						
			Silver Recovery	Ion Exchange	Reverse Osmosis	Ferricyanide Bleach Regeneration	$FeSO_4$ Precipitation	Dichromate Treatment	Reduction of Wastewater by Evaporation
<93 (<1,000)	<A	9,900	*	0	0	*	0	0	0
93-186 (1,000-2,000)	A	200	95	2	0	50	0	0	0
186-464 (2,000-5,000)	B	305	100	8	0	60	0.3	0	0
464-4,640 (5,000-50,000)	C	200	100	2	0	90	3	0	0
4,640- ∞ (50,000-∞)	D	15	100	20	33	95	20	0	7

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* Insufficient information to make reasonable estimate.

color reversal (DC) film recover and reuse color couplers from the developers. The following sections give brief accounts of both bleach regeneration and silver recovery techniques in current use and present information on their capability of reducing wastewater loadings. Developer regeneration and coupler recovery result in potential reduction of TOC in the raw waste. For those plants processing color paper containing cadmium compounds, developer regeneration also has the potential for reduction of cadmium in the raw waste. Insufficient data are available to quantify this reduction.

Bleach Regeneration

Bleach regeneration is used in the industry to reprocess ferricyanide bleach, EDTA bleach and bleach-fixes. The environmental benefits of using these techniques are discussed below.

Tables VII-2 through VII-4 show the environmental benefits of ferricyanide bleach regeneration and summarize the combined data obtained during the study. The data presented in these tables and the succeeding tables in this section have been extracted from the data tables in Section V and grouped according to the indicated plant characteristics. Some of the plants, for which cyanide values are given in the Section V effluent data tables, are not included in Tables VII-2 through VII-4. The available information from the plants not included was insufficient to allow a determination of the particular bleach treatment category. The production normalized total cyanide values reported are based on the areas of product processed with ferricyanide bleaches. These data are plotted as a cumulative distribution in Figures VII-1 through VII-3. Cumulative distribution plots are used here to show trends or grouping of data. Sudden changes in slope or discontinuities in the data displayed in such a plot indicate that the data groups may belong to different populations.

Considerably lower total cyanide effluent levels result from the use of regeneration methods. An additional benefit results in the treatment of the waste fix by ferrous sulfate ($FeSO_4$) precipitation as shown in Table VII-4. It should be noted that the fix waste is treated and discharged in batches at the listed plants. The plant effluents represented in Table VII-4 do not contain any treated waste fix batches. However, data taken from plant 4550's fix blowdown indicate that the treated waste contributes 0.9 percent of the total cyanide waste load. The processing and controls used in all plants listed in the table are comparable to 4550.

EDTA based bleach fixes are also regenerated within the industry. The benefits here are similar to those described earlier for the ferricyanide bleaches (i.e., a reduction of pollutant raw waste loading and a saving of processing raw materials).

Dichromate based bleaches are not regenerated as such in this industry. Some plants reconstitute waste dichromate bleach by discharging about 50 percent of the waste and reconstitute the remainder by chemical addition.

TABLE VII-2
Total Cyanide Content in Plant Effluent of Plants Using Ferricyanide Bleach with No Regeneration

Plant	Total cyanide load, kg/1,000 sq m (lb/1,000 sq ft)
0201	8.3 (1.7)
0204	23 (4.8)
0205	48 (9.8)
0210	21 (4.3)
0218	13 (2.6)
0229	18 (3.6)
	Av = 22 (4.5)

TABLE VII-3

Total Cyanide Content in Effluent of Plants Using Ferricyanide Bleach Regeneration

Plant	Total cyanide load, kg/1,000 sq m (lb/1,000 sq ft)
0215	4.4 (0.90)
0223	7.3 (1.5)
1465	7.3 (1.5)
2714	8.3 (1.7)
6208*	0.78 (0.16)
8226*	0.63 (0.13)
	Av = 4.8 (0.98)

* These plants are movie labs. Plant 6208 uses "replenish on demand" system for ferricyanide bleaches.

TABLE VII-4

Total Cyanide Content in Effluent of Plants Using Ferricyanide Bleach Regeneration plus $FeSO_4$ Precipitation Treatment on Waste Fix

Plant	Amount, kg/1,000 sq m (lb/1,000 sq ft)
0232	1.3 (0.26)
0233	0.59 (0.12)
0234	2.6 (0.53)
0235	1.4 (0.28)
0236	0.59 (0.12)
0237	1.4 (0.28)
2465	1.0 (0.21)
2488	0.39 (0.08)
3437	0.26 (0.054)
4228	1.4 (0.28)
4550	0.54 (0.11)
4666	1.7 (0.34)
5552	1.9 (0.39)
6726	0.76 (0.16)
	Av = 1.1 (0.23)

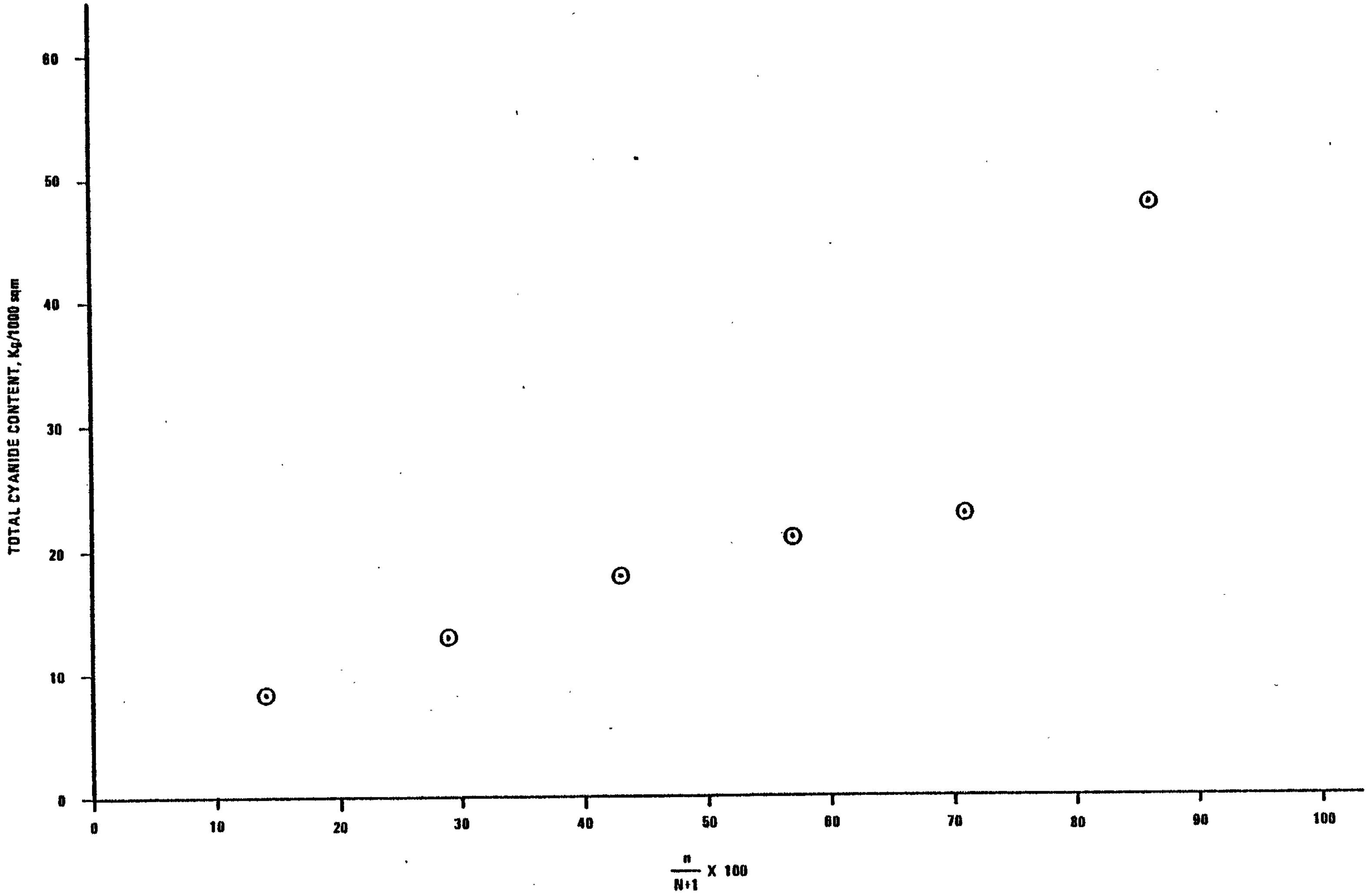

FIGURE VII-1 TOTAL CYANIDE CONTENT IN EFFLUENT – NO BLEACH REGENERATION

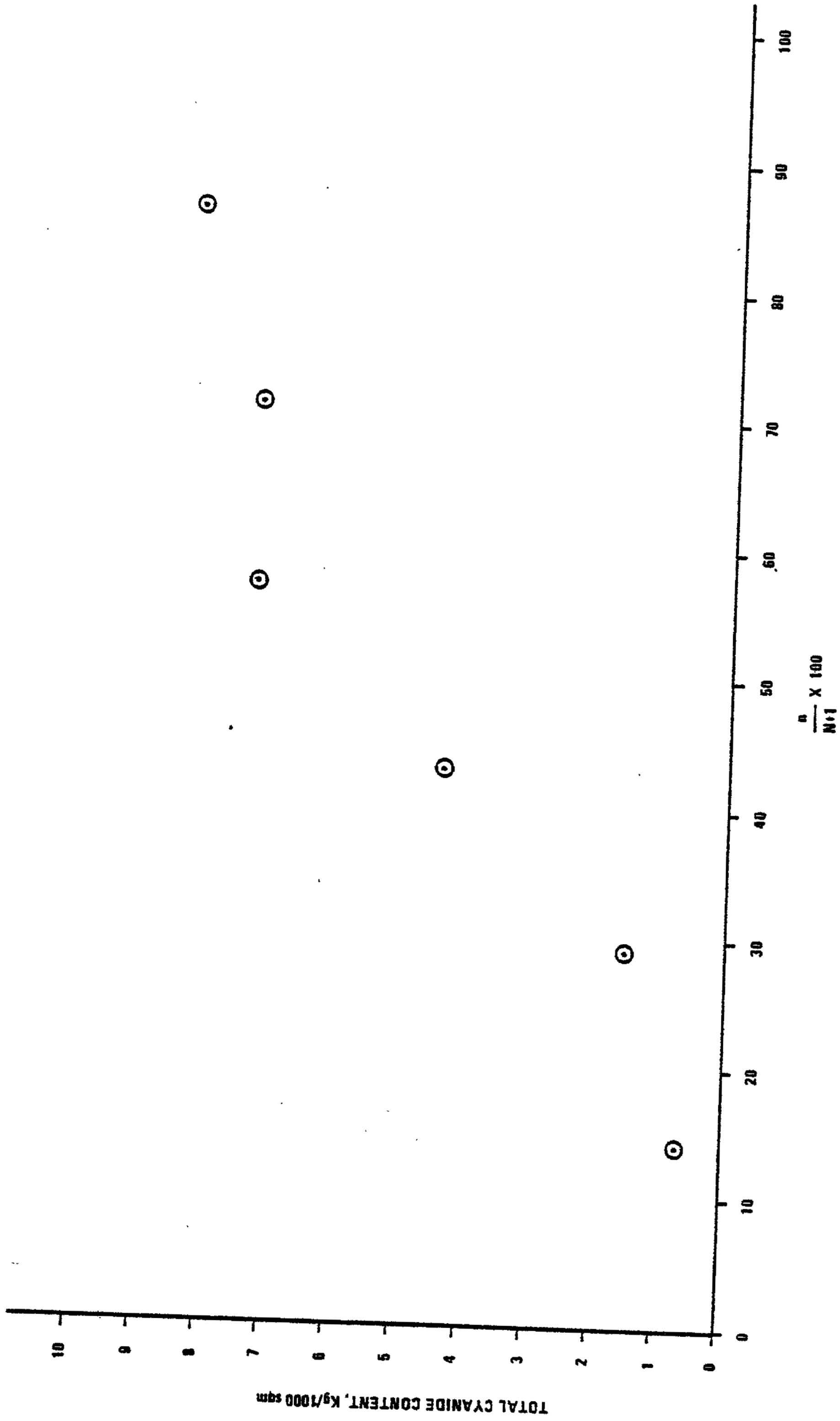

FIGURE VII-2 TOTAL CYANIDE IN EFFLUENT – PLANT USING BLEACH REGENERATION

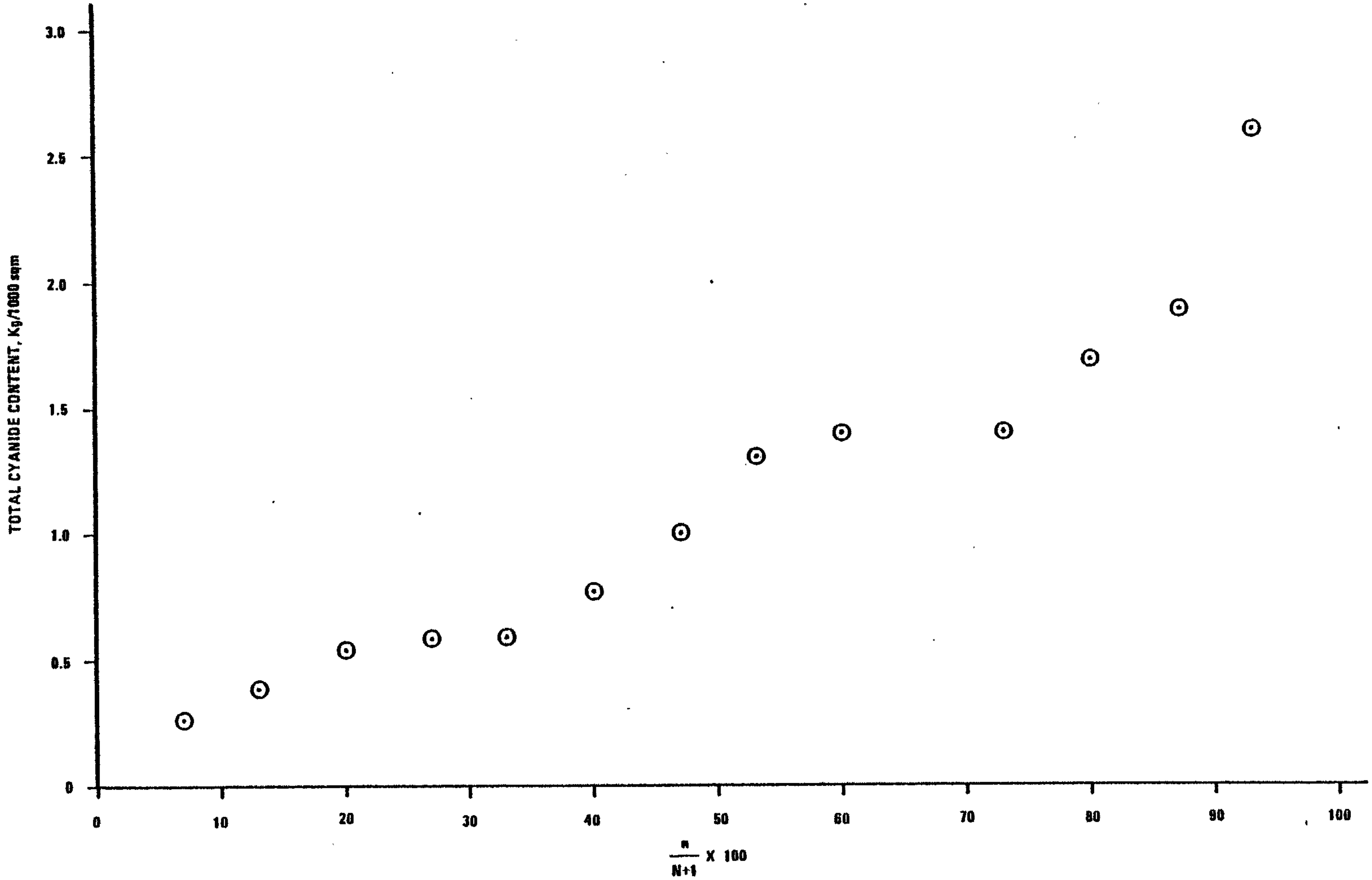

FIGURE VII-3 TOTAL CYANIDE IN EFFLUENT – BLEACH REGENERATION AND FERROUS SULFATE PRECIPITATION

Silver Recovery

There are at least five methods in current use for recovery of silver from photographic processing solutions. These are metallic replacement, electrolytic plating, ion exchange, reverse osmosis, and chemical precipitation.

Tables VII-5 through VII-7 display the environmental benefits of silver recovery and summarize the information obtained. Some of the plants, for which silver values are given in the Section V effluent data tables, are not included in Tables VII-5 through VII-7. The available information from these plants was insufficient to allow a determination of the particular silver recovery category. The production normalized total silver values reported are based on the area of all material processed. These data are plotted as a cumulative distribution in Figures VII-4 through VII-6. A considerable reduction in the amount of silver in the plant effluent is achieved by the use of standard metallic replacement and electrolytic plating silver recovery processes.

The group of plants shown in Table VII-7 and Figure VII-6 either hold waste fix in holding tanks pending batch discharge or contractor haul the waste fix. As a result, the effluent samples taken from these plants contain no waste fix. The silver amount in the effluent from these plants is attributed to carryover of silver into the after-fix wash. The average quantity of silver (0.11 kg/1,000 sq m) in the effluent of the plants included in Table VII-7 supports the average silver quantity (0.14 kg/1,000 sq m) for the plants included in Table VII-6 when the relative amounts of silver in the fix after silver recovery and the wash water are considered. Although contractor hauling potentially results in reduced plant effluent silver levels, the hauled fix must be disposed of in an environmentally sound manner for this to be a net environmental benefit.

Additional reduction of discharged silver can be achieved by the use of ion exchange or reverse osmosis and chemical precipitation in addition to the standard processes as shown in Table VII-8. At present, most of the industry uses metallic replacement and electrolytic plating recovery methods. Ion exchange, reverse osmosis, and precipitation methods are used only at a few sites and then, generally, in addition to the other methods.

TABLE VII-5
Results of Silver Recovery on Silver Content in Plant Effluent - No Silver Recovery on Some Processes

Plant	Total silver load, kg/1,000 sq m (lb/1,000 sq ft)
0204	0.47 (0.096)
0205	1.0 (0.21)
0209	0.54 (0.11)
0218	1.4 (0.29)
0223	0.25 (0.051)
0227	0.88 (0.18)
0228	0.034 (0.007)
0229	0.83 (0.17)
0230	0.78 (0.16)
	Av = 0.68 (0.14)

TABLE VII-6
Results of Silver Recovery on Silver Content in Plant Effluent - Silver Recovery on All Processes

Plant	Total silver load, kg/1,000 sq m (lb/1,000 sq ft)
0201	0.12 (0.025)
0202	0.17 (0.034)
0203	0.22 (0.045)
0210	0.088 (0.018)
0211	0.17 (0.034)
0213	0.21 (0.044)
0214	0.037 (0.0075)
0220	0.054 (0.011)
0221	0.34 (0.07)
0224	0.073 (0.015)
0225	0.15 (0.031)
0226	0.23 (0.048)
0232	0.13 (0.027)
0233	0.049 (0.010)
1421	0.27 (0.055)
1465	0.13 (0.026)
2146	0.32 (0.066)
2714	0.063 (0.013)
5120	0.0013 (2.6 x 10^{-4})
8226	0.054 (0.011)

Av = 0.14 (0.029)

TABLE VII-7
Results of Silver Recovery on Silver Content in Plant Effluent - Silver Recovery on All Waste Fix But Waste Fix Not in Sample

Plant	Total silver load, kg/1,000 sq m (lb/1,000 sq ft)
0021	0.16 (0.032)
0206	0.059 (0.012)
0234	0.059 (0.012)
0235	0.19 (0.039)
0236	0.088 (0.018)
0237	0.14 (0.028)
0662	0.12 (0.025)
1635	0.25 (0.052)
2465	0.088 (0.018)
2488	0.10 (0.021)
3437	0.028 (0.0058)
3630	0.043 (0.0089)
4228	0.14 (0.028)
4550	0.078 (0.016)
4666	0.068 (0.014)
5552	0.059 (0.012)
6174	0.054 (0.011)
6582	0.13 (0.026)
6726	0.17 (0.034)
	Av = 0.11 (0.022)

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